



## DECLARATION

I, Kazuhiko OGAWA, residing at 5-12-5, Inodai, Toride-shi, Ibaraki, Japan, hereby declare that I have a thorough knowledge of the English and Japanese languages and that the writing contained in the following pages is an accurate translation of the Japanese Priority Application Hei. 9-53583, filed on March 7, 1997.

Declared at Tokyo, Japan

This 21<sup>st</sup> day of September, 2000

Kazuhiko OGAWA

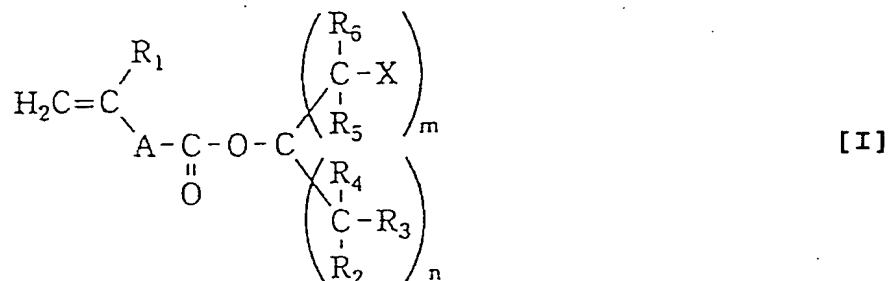
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[Name of document] SPECIFICATION

[Title of the invention] POSITIVE TYPE PHOTORESIST COMPOSITION  
FOR FAR ULTRAVIOLET RAY EXPOSURE

[Claims]

[Claim 1] A positive type photoresist composition for far ultraviolet ray exposure comprising a resin which is decomposed by action of an acid to increase solubility in an alkali solution, and a compound generating an acid by irradiation of an active light ray or radiation, wherein said resin is a polymer containing a monomer represented by the following general formula [I] as one of repeating structure units:



wherein  $\text{R}_1$  represents a hydrogen atom or a methyl group;  $\text{R}_2$  to  $\text{R}_4$ , which may be the same or different, each represents a hydrogen atom or an alkyl group;  $\text{R}_5$  and  $\text{R}_6$ , which may be the same or different, each represents a hydrogen atom, an alkyl group or a halogen atom;  $\text{X}$  represents a halogen atom;  $\text{A}$  represents one group selected

from the group consisting of a single bond, an alkylene group, a substituted alkylene group, an ether group, an ester group, a thioether group, a carbonyl group, an amido group, a sulfonamido group, a urethane group and a urea group, or a combination of two or more of them; and m is 1, 2 or 3, n is 0, 1 or 2, and the sum of m and n is 3.

[Claim 2] The positive type photoresist composition described in claim 1, wherein said resin is a copolymer containing repeating units of a monomer represented by general formula [I] and a monomer having an alicyclic hydrocarbon moiety in its molecule.

[Claim 3] The positive type photoresist composition described in claim 1 or 2, wherein the active light ray or the radiation for exposure has a wavelength of 170 nm to 220 nm.

[Claim 4] The positive type photoresist composition described in claim 1 or 2, wherein said resin further contains repeating structure units each having a group which is decomposed by action of an acid to increase solubility in an alkali developing solution.

[Claim 5] The positive type photoresist composition described in claim 1 or 2, wherein said composition is composed so as to give a transmission optical density of 1.0 or less per micron of coated layer in thickness to an active light ray having a wavelength of 193 nm.

[Detailed explanation of the invention]

[Technical field to which the invention pertains]

The present invention relates to an ultramicro-lithography process or another photofabrication process for producing a very large scale integrated circuit or a high capacity microchip, and more particularly to a positive type photoresist composition which can form a highly refined pattern by use of far ultraviolet rays including excimer laser beams.

[Prior art]

In photofabrication processes of lithography, the production of semiconductors for ICs and the production of circuit substrates for thermal heads, semiconductor wafer, glass, ceramic or metal substrates are coated with photoresists to a thickness of 0.5  $\mu\text{m}$  to 2.5  $\mu\text{m}$  by spin coating or roller coating, followed by heating and drying. Then, circuit patterns are printed thereon through exposure masks with active light such as ultraviolet rays, and baked after exposure if necessary, followed by development to form images of the resists. Further, pattern processing can be performed on the substrates by etching using the images as masks.

In many cases, alkali-soluble resins and photosensitive materials are generally used in combination as positive type photoresist compositions, and especially, compositions comprising novolak type phenol resins and naphthoquinone-diazide compounds in combination are used. The positive type photoresists

comprising the novolak resins and quinonediazide compounds have advantageous characteristics such as high resistance to plasma etching, the prevention of dissolution of the naphthoquinonediazide compounds, the disappearance of the ability of preventing the compounds from being dissolved, associated with carboxylic acids by light irradiation, and an improvement in alkali solubility of the novolak resins as a result thereof. Accordingly, a number of the photoresists have been developed and have come in practice, and sufficient results have been obtained for processing of a line width up to about 0.8  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

However, integrated circuits have been progressively increased in their integration degree, and therefore processing of ultrafine patterns having a line width of a half micron or less has become necessary in the production of semiconductor substrates for very large scale integrated circuits. For fulfilling this necessity, the wavelength of light used in exposure devices employed for photolithography becomes progressively shorter, and now, of the far ultraviolet rays, the use of excimer laser light having a short wavelength (such as XeCl, KrF or ArF) has been studied.

In the pattern formation of lithography in this wavelength region, the absorption of the novolak resins and the naphthoquinonediazide compounds in the far ultraviolet region is so strong that light becomes difficult to arrive at the bottom

portions of the resists. Accordingly, only patterns low in sensitivity and tapered are obtained. The novolak-naphthoquinonediazide resists are therefore insufficient.

One means for solving this problem is chemical amplification system resist compositions described in U.S. Patent 4,491,628 and European Patent 249,139. The positive type chemical amplification system resist composition is a composition designed so as to produce an acid in an exposed area by irradiation of active light such as far ultraviolet rays and to change the solubility of the area irradiated with active light and an area not irradiated therewith in a developing solution by a reaction using this acid as a catalyst, thereby forming a pattern on a substrate.

Examples of such resins which are used in combination with the photo acid generators and changed in solubility with the acids include acetal or O,N-acetal compounds (JP-A-48-89003), orthoesters or amidoacetal compounds (JP-A-51-120714), polymers having acetal or ketal groups on main chains (JP-A-53-133429), enol ether compounds (JP-A-55-12995), N-acyliminocarboxylic acid compounds (JP-A-55-126236), polymers having orthoester groups on main chains (JP-A-56-17345), tertiary alkyl ester compounds (JP-A-60-3625), silyl ester compounds (JP-A-60-10247) and silyl ether compounds (JP-A-60-37549 and JP-A-60-121446). These compounds exceed 1 in quantum yield in principle, so that they

exhibit high photosensitivity.

Similarly, the systems which are stable at room temperature, but are decomposed in the presence of acids by heating to be solubilized in alkalis include, for example, combined systems of photoacid generators described in JP-A-59-45439, JP-A-60-3625, JP-A-62-229242, JP-A-63-27829, JP-A-63-36240 JP-A-63-250642, Polym. Eng. Sci., 23, 1012 (1983), ACS. Sym., 242, 11 (1984), Semiconductor World, November, 91 (1987), Macromolecules, 21, 1475 (1988) and SPIE, 920, 42 (1988), and esters of tertiary or secondary carbon (for example, t-butyl or 2-cyclohexenyl) or carbonic ester compounds. These systems also have high sensitivity and can be effective for the above-mentioned shortening of the wavelength of light sources, because of their lower absorption in the far ultraviolet region, compared with the novolak resin/naphthoquinonediazide systems.

In particular, there are proposed resist compounds comprising hydroxystyrene polymers particularly low in photoabsorption when the 248-nm light of a KrF excimer laser is used, into which acetal groups or ketal groups are introduced as protective groups. Examples thereof are described in JP-A-2-141636, JP-A-2-19847, JP-A-4-219757 and JP-A-5-281745.

Besides, similar compositions having t-butoxycarbonyloxy groups or p-tetrahydropyranyloxy groups as acid decomposable groups are proposed in JP-A-2-209977, JP-A-3-206458 and JP-A-2-19847.

However, these compositions substantially have the disadvantage

of low sensitivity caused by too high absorbance when an ArF laser is used as a light source. Accompanied thereby, they further have the problems of deterioration of pattern profiles and lack of focus permissibility, so that many improvements are required.

As the photoresist compositions for the ArF light source, photoresist compositions in which (meth)acrylic resins smaller in absorption than partially hydrogenated hydroxystyrene resins are combined with compounds generating acids with light are proposed, for example, in JP-A-7-199467 and JP-A-7-252324. Above all, JP-A-6-289615 discloses resins in which organic groups of tertiary carbon are attached by ester linkages to oxygen of a carboxyl group of acrylic acid, and JP-A-7-234511 discloses copolymer resins comprising structural units in which dimethyl-substituted tertiary carbon groups are attached by ester linkages to oxygen of a carboxyl group of acrylic acid, and structural units in which alicyclic groups are attached by ester linkages. These resins have photoabsorptive aryl groups in carbon substituent groups, or are poor in acid decomposability although improved in light permeability to the ArF light source. Thus, resins exhibiting characteristics sufficiently satisfactory to the object have not been obtained yet.

[Problem to be solved by the invention]

It is therefore an object of the present invention is to develop a photoresist composition having an acid decomposable group to which the above-mentioned tertiary carbon atom is attached



by an ester linkage, which is improved in the prior-art disadvantages, namely low in absorbance and good in acid decomposability, therefore high in sensitivity, good in a pattern profile and excellent in storage stability, to an ArF excimer laser light source.

[Means to solve the problem]

The present inventors have intensively studied materials constituting resist compositions in positive type chemical amplification systems. As a result, the present inventors have known that the objects can be attained by a combination of a (meth)acrylic resin containing structural units each having an acid decomposable substituent group of a specific structure and a photo acid generator, thus completing the present invention.

That is, the above-mentioned objects can be attained by the following constitution:

1. A positive type photoresist composition for far ultraviolet ray exposure comprising a resin which is decomposed by action of an acid to increase solubility in an alkali solution, and a compound generating an acid by irradiation of an active light ray or radiation, wherein said resin is a polymer containing a monomer represented by the following general formula [I] as one of repeating structural units:



in the above 1 or 2, wherein the active light ray or the radiation for exposure has a wavelength of 170 nm to 220 nm.

4. The positive type photoresist composition described in the above 1 or 2, wherein said resin further contains repeating structural units each having a group which is decomposed by action of an acid to increase solubility in an alkali developing solution.

5. The positive type photoresist composition described in any one of the above 1 to 3, wherein said composition is composed so as to give a transmission optical density of 1.0 or less per micron of coated layer in thickness to an active light ray having a wavelength of 193 nm.

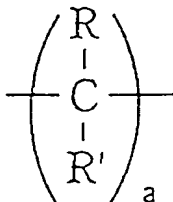
[Mode for carrying out the invention]

The present invention will be described in detail below.

First, the resins which are decomposed by the action of acids to increase solubility in alkali developing solutions, namely the polymers containing the repeating structural units represented by general formula [I], are described. In general formula [I],  $R_1$  represents a hydrogen atom or a methyl group;  $R_2$  to  $R_4$ , which may be the same or different, each represents a hydrogen atom or an alkyl group;  $R_5$  and  $R_6$ , which may be the same or different, each represents a hydrogen atom, an alkyl group or a halogen atom; and X is a halogen atom. The alkyl groups represented by  $R_2$  to  $R_6$  are preferably lower alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and sec-butyl, more preferably methyl, ethyl, propyl, isopropyl and

butyl, and most preferably methyl and ethyl. X is a chlorine, bromine or iodine ion. m is 1, 2 or 3, n is 0, 1 or 2, and the sum of m and n is 3.

A represents one group selected from the group consisting of a single bond, an alkylene group, a substituted alkylene group, an ether group, an ester group, a thioether group, a carbonyl group, an amido group, a sulfonamido group, a urethane group and a urea group, or a combination of two or more of them. The alkylene groups and the substituted alkylene groups represented by A include groups shown below:

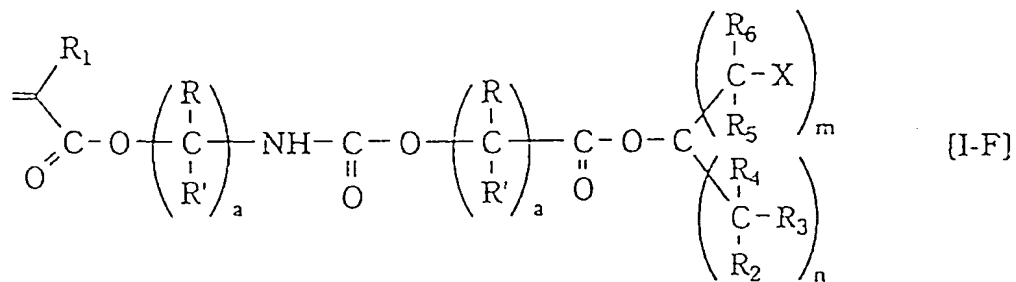
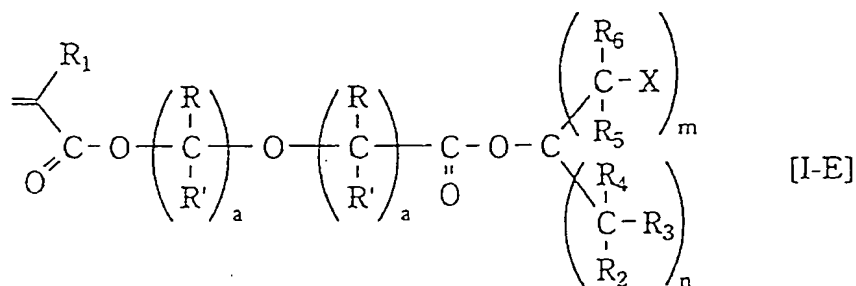
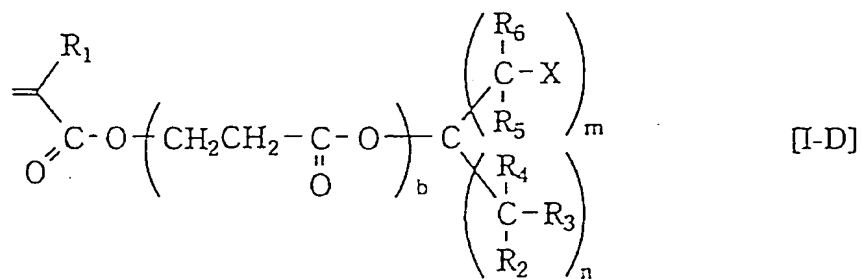
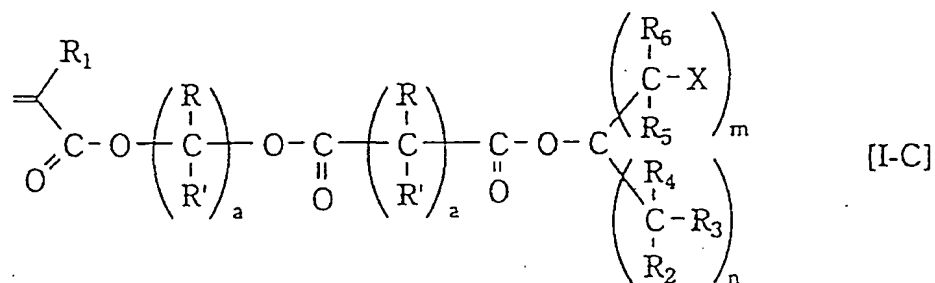
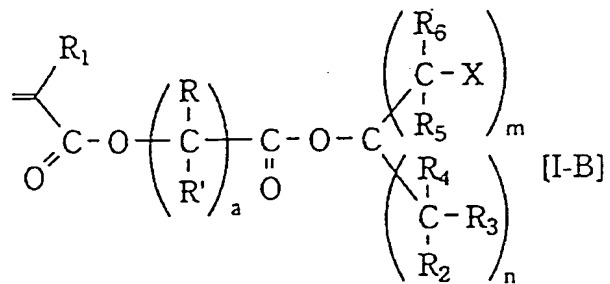
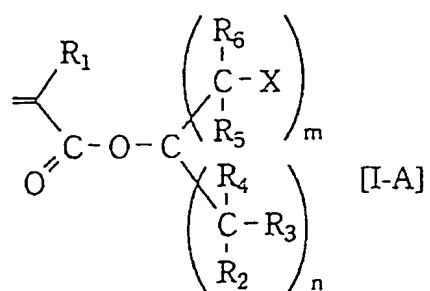


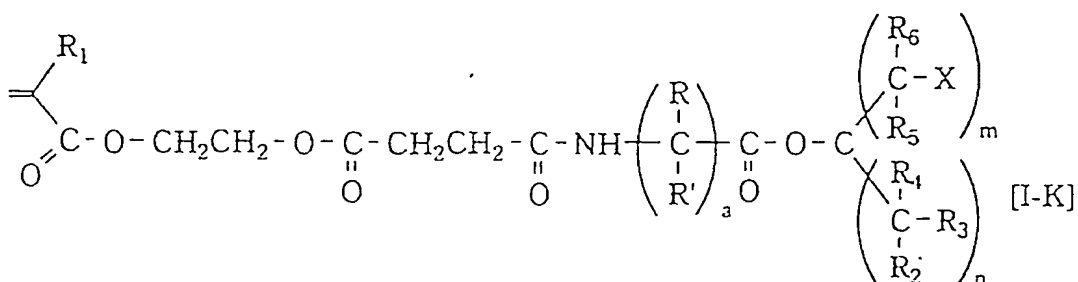
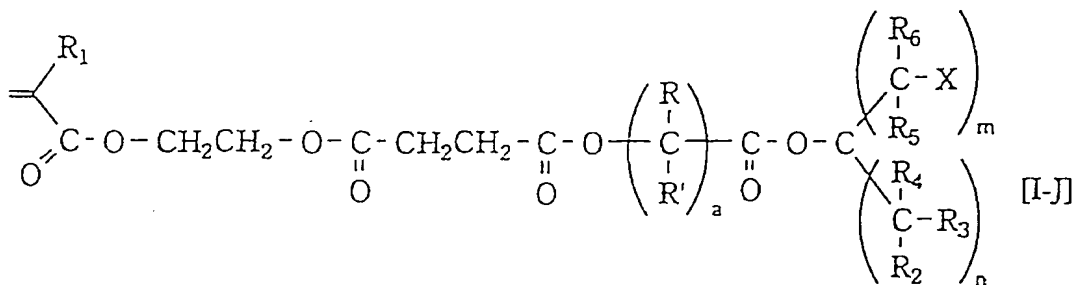
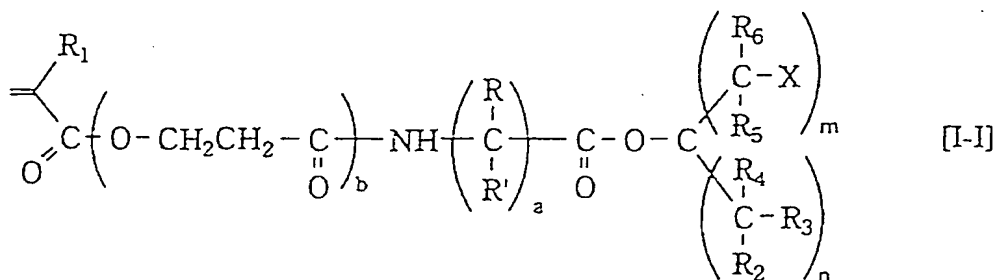
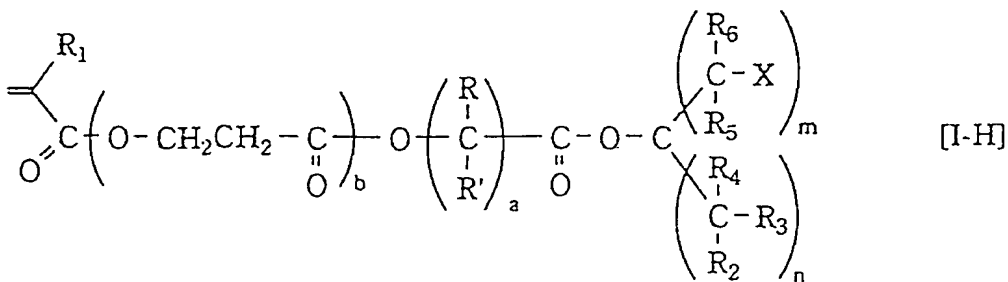
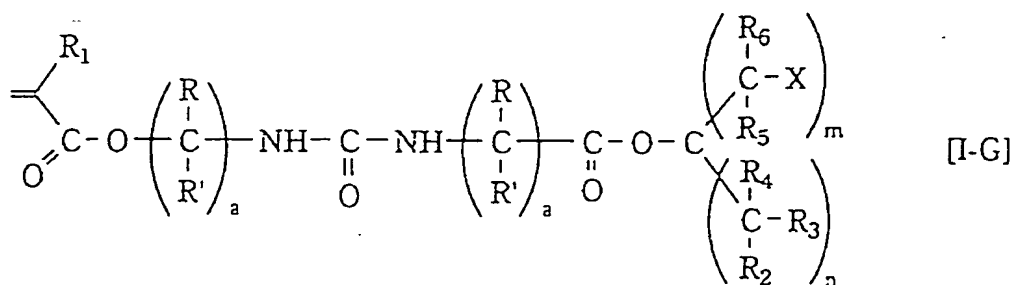
wherein R and R', which may be the same or different, each represents a hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, a hydroxyl group or an alkoxy group. The alkyl groups are preferably lower alkyl groups such as methyl, ethyl, propyl, isopropyl and butyl, and more preferably, methyl, ethyl, propyl and isopropyl. Substituent groups of the substituted alkyl groups include halogen atoms and hydroxyl and alkoxy groups.

The alkoxy groups include groups having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and butoxy. n represents an integer of 1 to 10.

Of the above, A is particularly preferably a single bond, or one group selected from an alkylene group, a substituted alkylene group, an amido group, a urethane group, a urea group, an ether group and an ester group, or a combination of two or more of them. The alkylene groups and the substituted alkylene groups are preferably alkylene groups each having 1 to 4 carbon atoms herein, and specific examples thereof include methylene, ethylene, propylene, butylene, methyl-substituted methylene, dimethyl-substituted methylene, methyl-substituted ethylene, dimethyl-substituted ethylene, methyl-substituted propylene and dimethyl-substituted propylene.

Preferred examples of the monomers represented by general formula [I] include monomers represented by the following general formulas [I-A] to [I-K]:

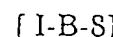
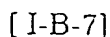
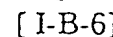
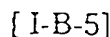
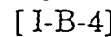
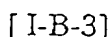
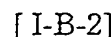
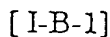
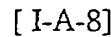
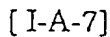
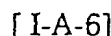
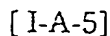
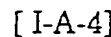
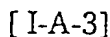
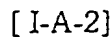
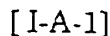


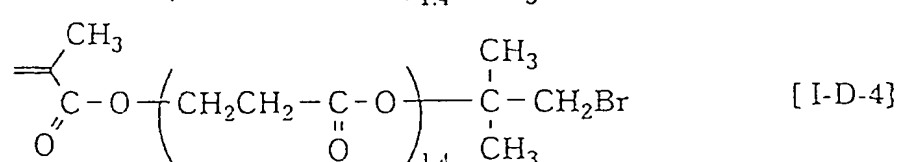
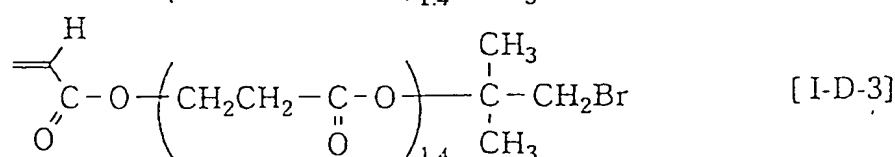
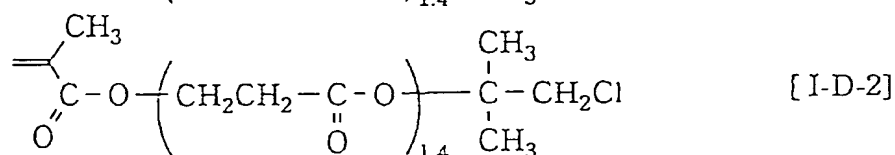
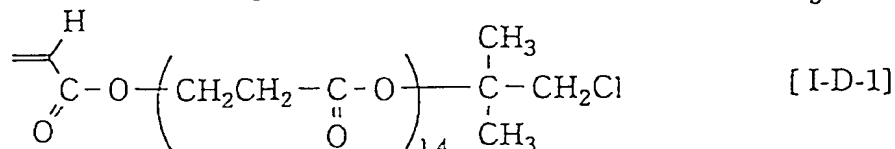
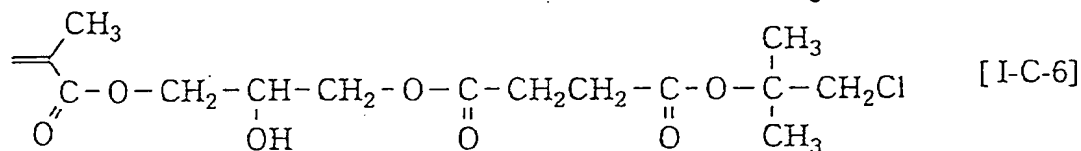
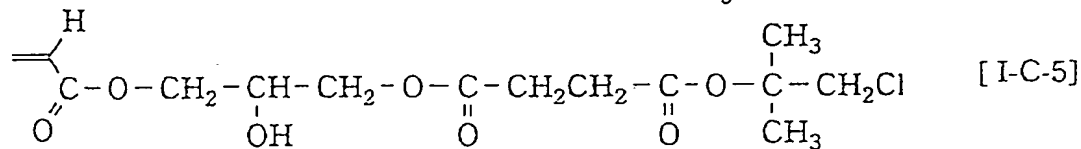
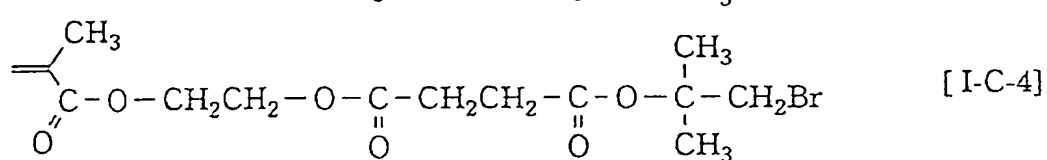
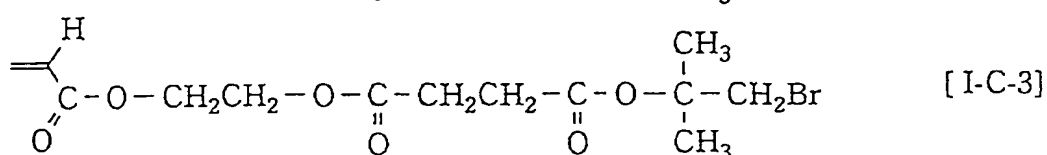
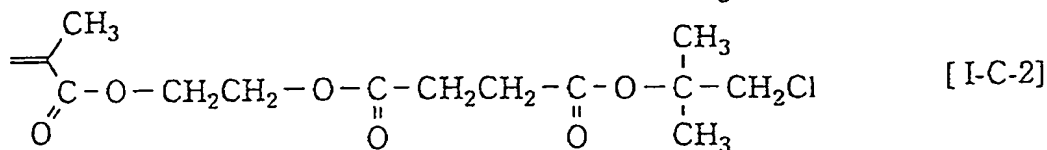
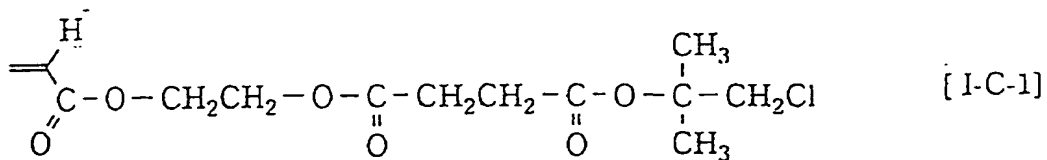


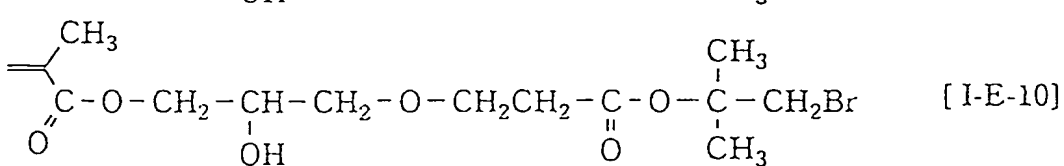
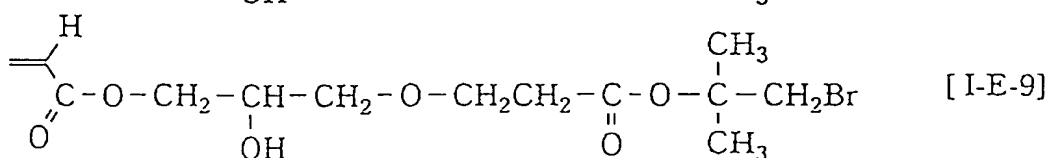
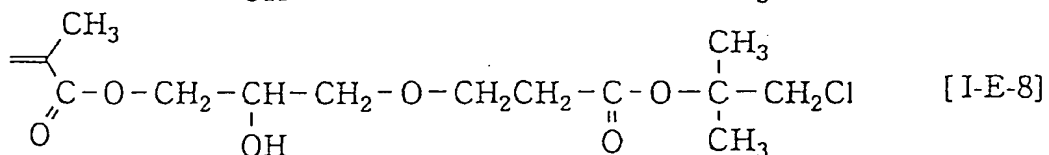
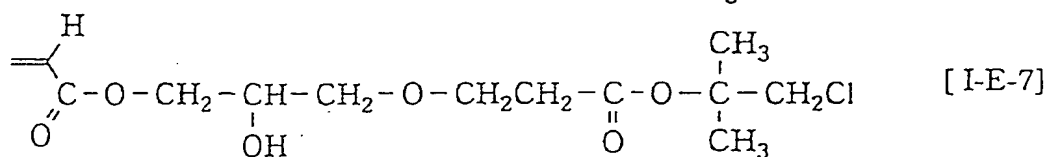
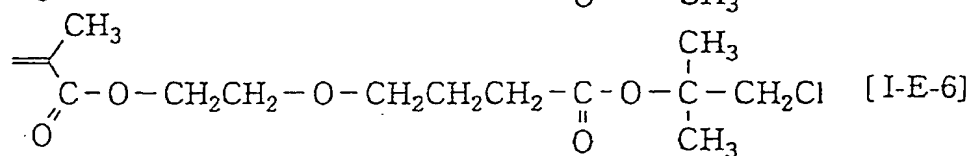
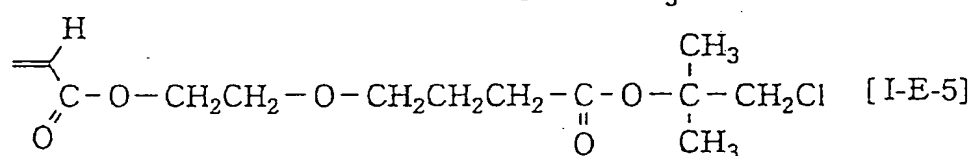
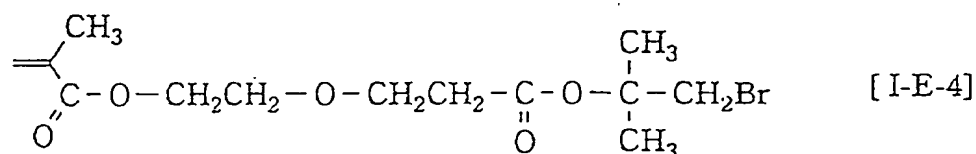
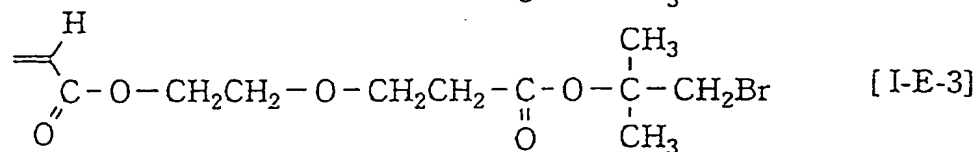
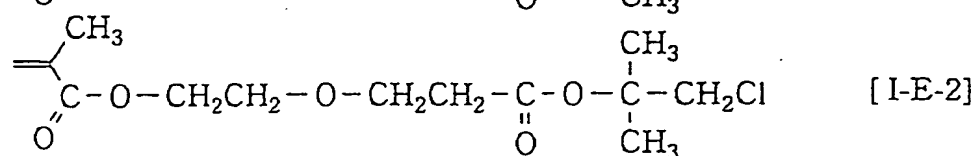
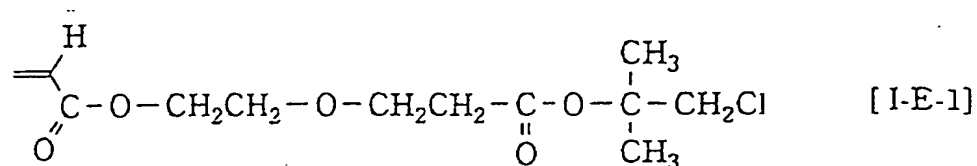
In the above-mentioned general formulas,  $R_2$  to  $R_7$ ,  $R$ ,  $R'$ ,  $n$  and  $m$  have the same meanings as given above, and  $a$  and  $b$  each represents an integer of 1 or 2.

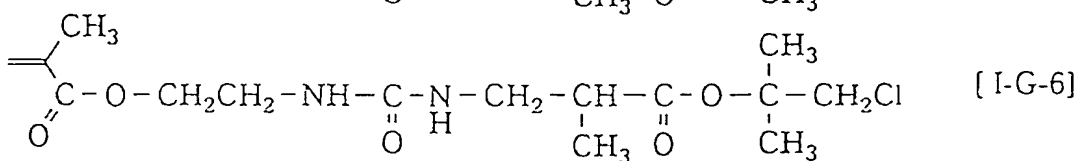
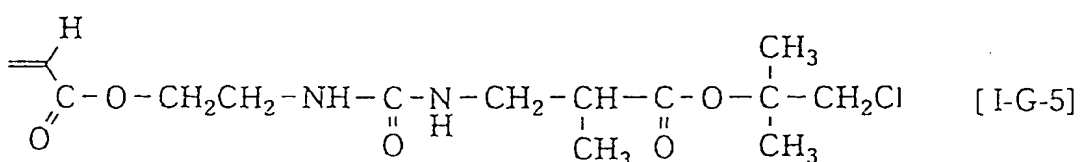
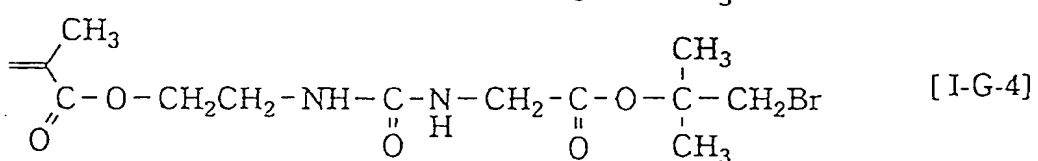
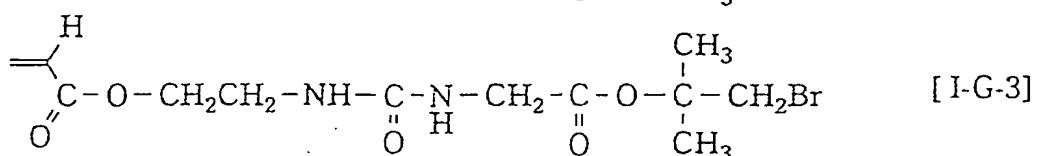
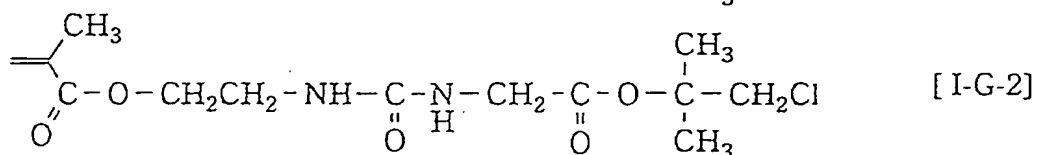
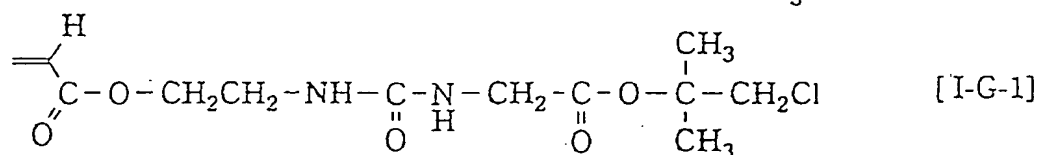
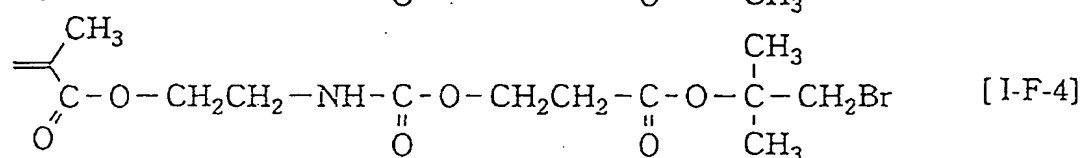
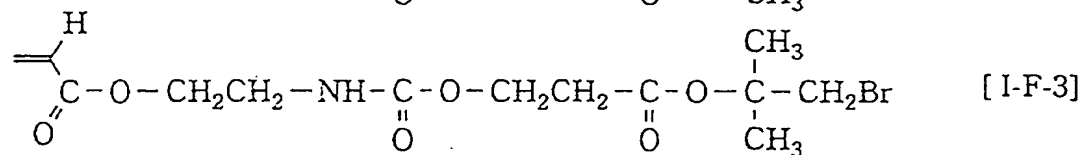
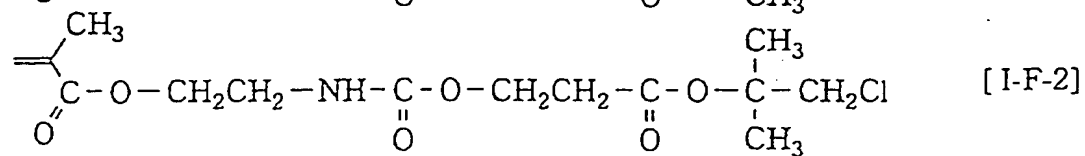
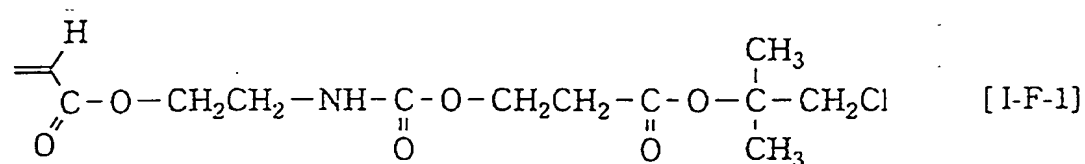
Specific examples of the monomers represented by general formula [I] are enumerated below, but do not limit the scope of the present invention:

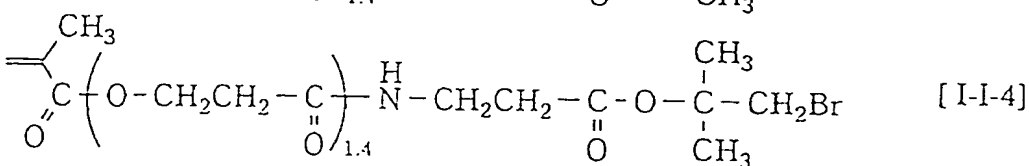
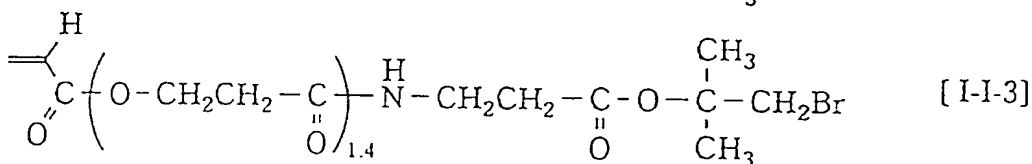
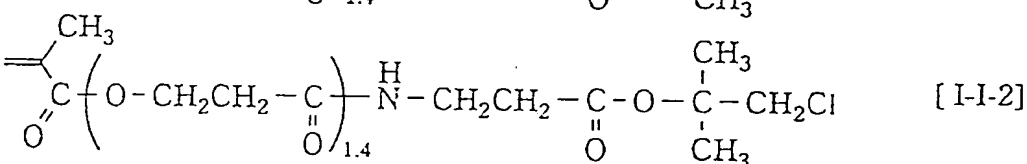
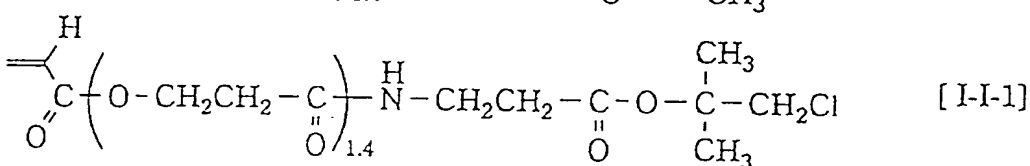
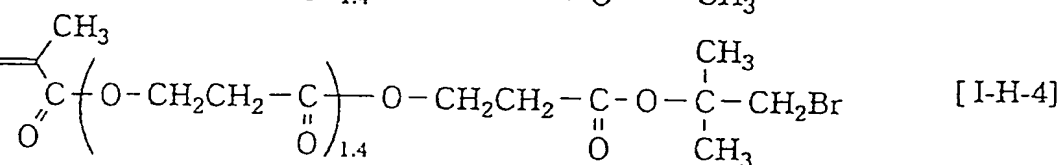
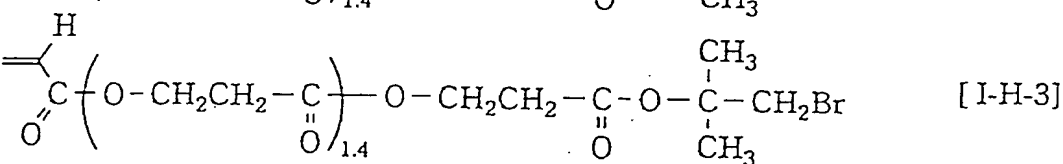
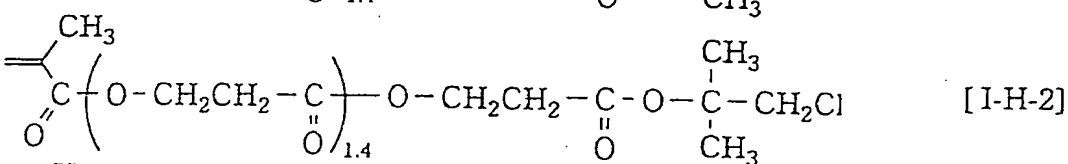
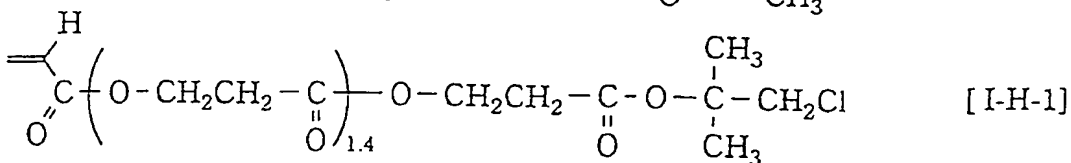
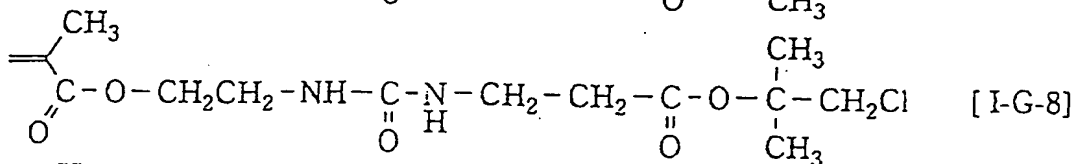
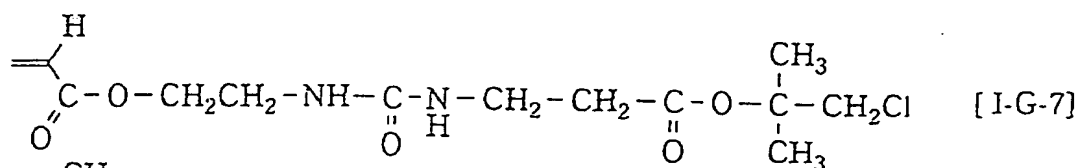


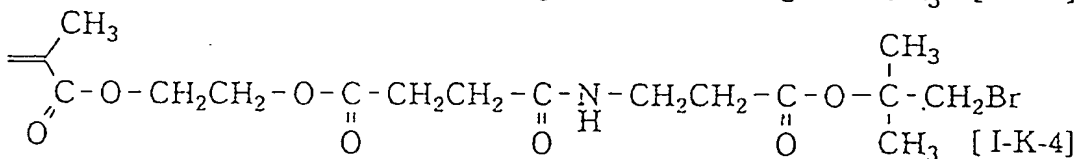
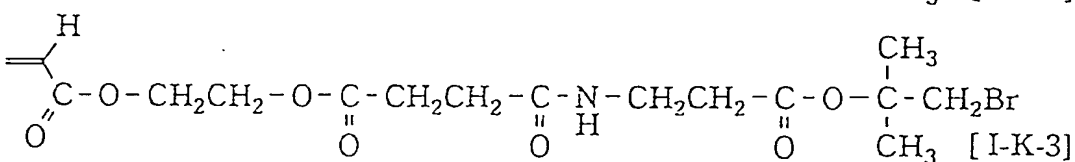
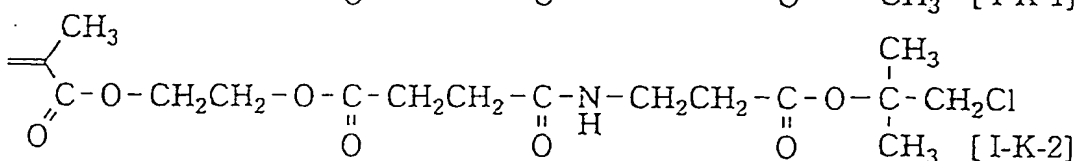
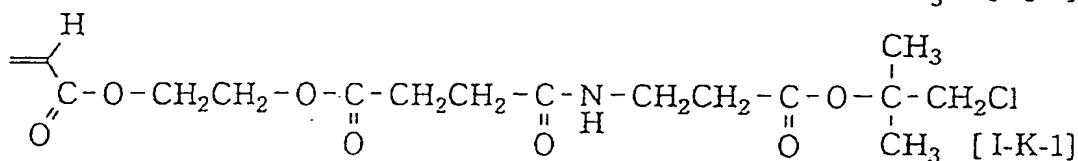
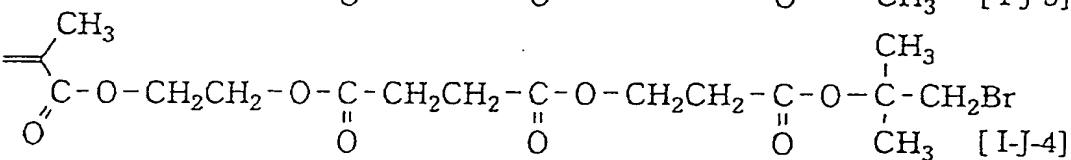
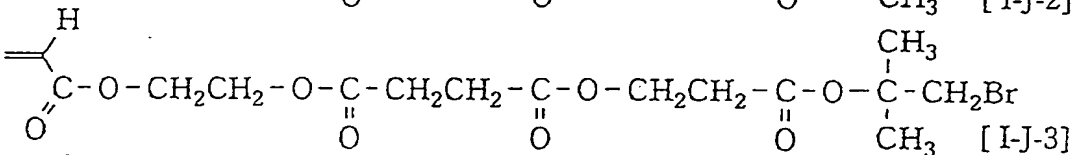
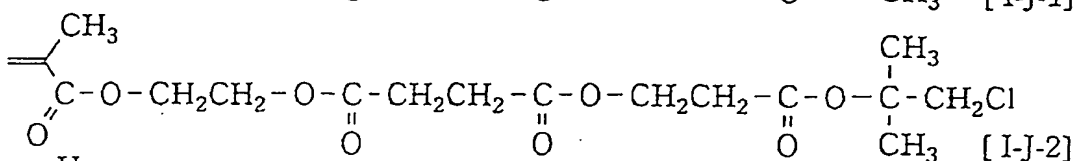
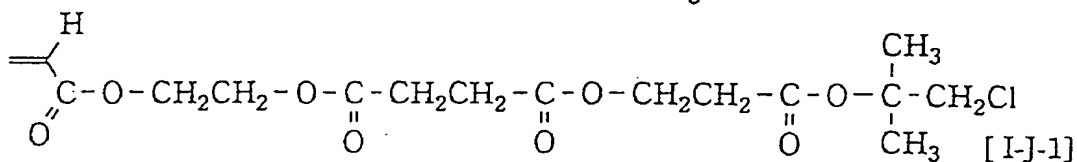
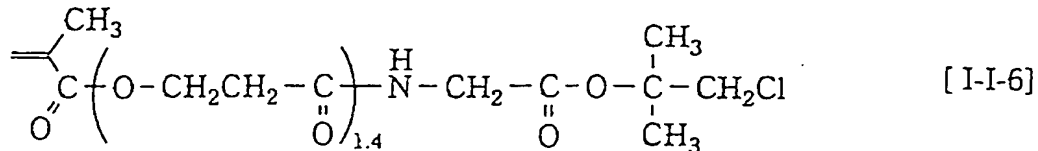
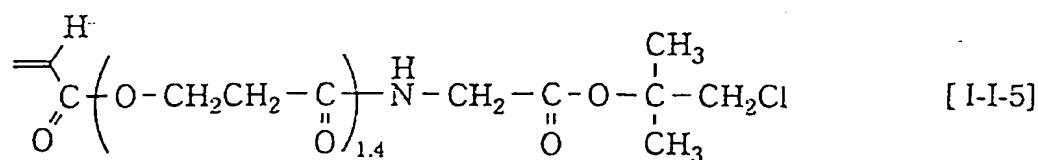


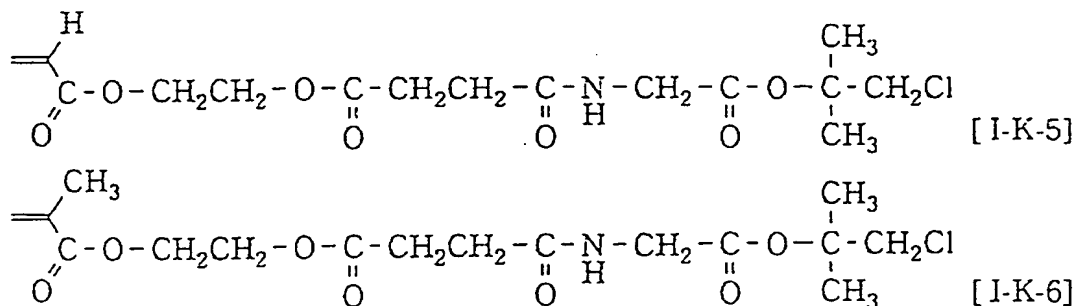






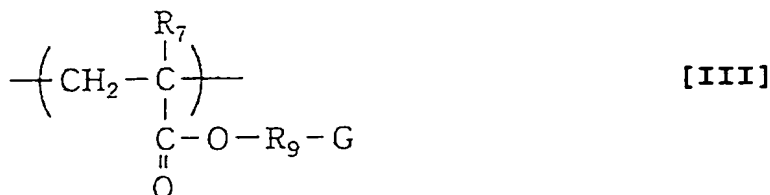
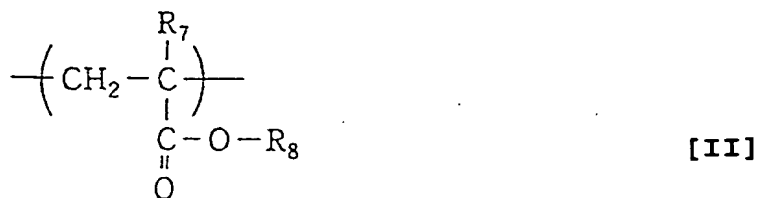






Such monomers represented by general formula [I] can be synthesized by esterifying carboxylic acids having radical-polymerizable carbon-carbon bonds in their molecules with 2-hydroxylactones by the method described in Angew. Chem. int. Ed. Engl., 17, 522 (1978), or by reacting the corresponding carboxylic acid chlorides with 2-hydroxylactones under basic conditions.

It is preferred that the resins used in the positive type photoresist compositions of the present invention contain the repeating units having alicyclic hydrocarbon moieties in their molecules, as well as the groups represented by the above-mentioned general formula [I]. This can enhance the resistance to dry etching of the positive photoresists. The repeating structural units having alicyclic hydrocarbon moieties in their molecules include, for example, repeating structural units represented by the following general formulas [II] and [III].



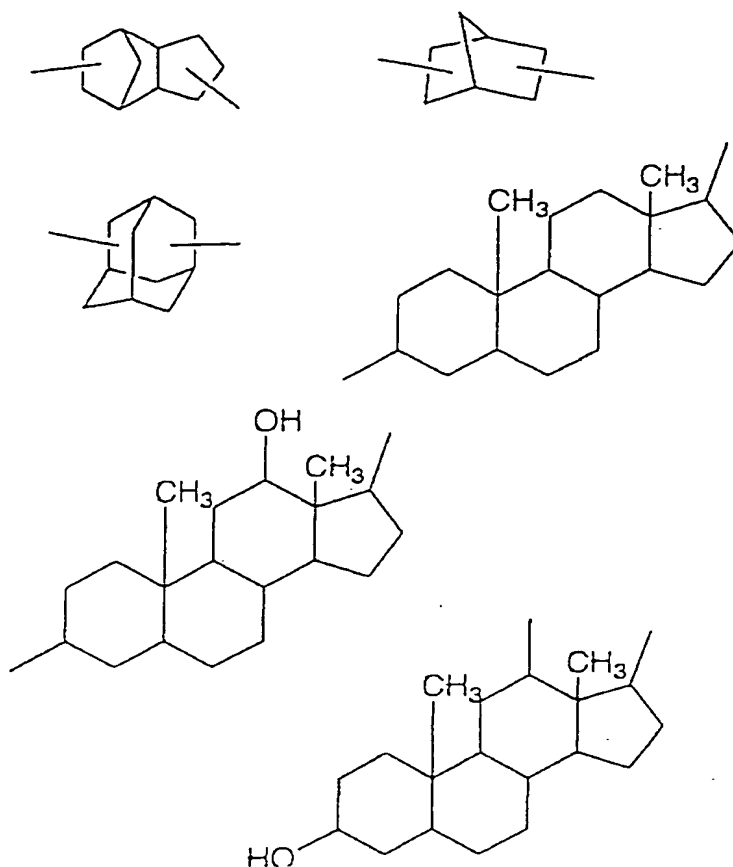
$\text{R}_7$  in general formula [II] is hydrogen atom or a methyl group.  $\text{R}_8$  is a monovalent alicyclic hydrocarbon group. Specifically, such groups include an adamantyl group, a 2-methyl-2-adamantyl group, a norbornyl group, a bornyl group, an isobornyl group, a tricyclo-decanyl group, a dicyclopentenyl group, a norbornaneepoxy group, a menthyl group, an isomenthyl group and a neomenthyl group.

In general formula [III],  $\text{R}_7$  is hydrogen atom or a methyl group as in general formula [II].  $\text{R}_9$  is a connecting group having a divalent alicyclic hydrocarbon moiety.  $\text{G}$  represents  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{COOR}_{10}$  or  $-\text{OR}_{10}$  wherein  $\text{R}_{10}$  represents a tertiary alkyl group, a tetrahydropyranyl group, a tetrahydrofuranyl group,  $-\text{CH}_2\text{OR}_{11}$



or  $-\text{CH}(\text{CH}_3)\text{OR}_{11}$  wherein  $\text{R}_{11}$  represents an alkyl group.

The alicyclic hydrocarbon moieties contained in the connecting groups represented by  $\text{R}_9$  include, for example, the following structures:



The connecting group in  $R_7$  connecting the above-mentioned alicyclic hydrocarbon moiety and the ester group, or above-mentioned alicyclic hydrocarbon moiety and the group represented by  $G$ , which may be a single bond, includes one group selected from an alkylene group, an ether group, a thioether group, a carbonyl group, an ester group, an amido group and a sulfonamide group, or a combination of two or more of them.

$R_8$  in the  $-COOR_8$  or  $-OR_8$  group represents a substituent group decomposable by the action of an acid. Examples of such

groups include tertiary alkyl groups such as t-butyl and t-amyl, 1-alkoxyethyl groups such as tetrahydropyranyl, tetrahydrofuranyl,  $-\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$  and  $-\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}(\text{CH}_3)_2$ , and alkoxymethyl groups such as  $-\text{CH}_2\text{OCH}_3$  and  $-\text{CH}_2\text{OCH}_2\text{CH}_3$ .

In the above-mentioned resins, the content of the repeating structural units containing the groups represented by general formula [I] is preferably 5 mol% to 80 mol%, and more preferably 10 mol% to 70 mol%, based on the total repeating units. Less than 5 mol% is unfavorable because the effect of the present invention is difficult to be achieved. Exceeding 80 mol% unfavorably results in liability to deteriorate the resistance to dry etching.

The content of the repeating structural units having alicyclic hydrocarbon moieties in their molecules contained in the resins is 20 mol% to 95 mol%, and preferably 30 mol% to 90 mol%, based on the total repeating units.

It is preferred that the above-mentioned resins used in the present invention further contain groups which are decomposed by the action of acids to increase solubility in alkali developing solutions (also referred to as acid decomposable groups), in addition to the groups represented by general formula [I] and the repeating structural units having alicyclic hydrocarbon moieties. This makes the effect of improving sensitivity more significant.

Preferred examples of such acid decomposable groups

include  $\text{-COOR}_{11}$ ,  $\text{-OR}_{11}$ , a 3-oxocyclohexyl group and a 2-oxocyclohexyl group as described above.

Specifically, examples thereof include repeating structural units corresponding to conventional monomers such as t-butylacrylate, t-butylmethacrylate, t-amylacrylate, t-amylmethacrylate, tetrahydrofuranyl acrylate, tetrahydrofuranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl methacrylate, alkoxymethyl acrylate, alkoxymethyl methacrylate, 1-alkoxyethyl methacrylate, 3-oxocyclohexyl acrylate, 3-oxocyclohexyl methacrylate, 2-oxocyclohexyl acrylate and 2-oxocyclohexyl methacrylate.

In the above-mentioned resins, the content of the repeating structural units corresponding to such conventional monomers having acid decomposable groups is preferably 99 mol% or less, more preferably 90 mol% or less, and most preferably 80 mol% or less, based on the total molar number of the repeating structural units having the groups represented by the above-mentioned general formula [I]. Exceeding 99 mol% is unfavorable because the effect of the present invention is not sufficiently manifested.

Such resins can be further copolymerized with the following monomers as repeating units within the range in which the effect of the present invention can be effectively obtained. However, the present invention is not limited thereto.

This enables fine adjustment of properties required for the above-mentioned resins, particularly (1) solubility in coating

solvents, (2) film forming properties (glass transition temperature), (3) alkali developing properties, (4) film thickness loss (hydrophilic and hydrophobic properties, selection of alkali-soluble groups), (5) adhesion of unexposed areas to substrates and (6) resistance to dry etching.

Such monomers for copolymerization include, for example, compounds each having one addition-polymerizable unsaturated bond, selected from acrylic esters, methacrylic esters, acrylamide compounds, methacrylamide compounds, allyl compounds, vinyl ethers and vinyl esters.

Specifically, examples of the acrylic esters include alkyl acrylates (wherein alkyl groups each preferably has 1 to 10 carbon atoms) (such as methyl acrylate, ethyl acrylate, propyl acrylate, t-butyl acrylate, amyl acrylate, cyclohexyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, chloroethyl acrylate, 2-hydroxyethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate and tetrahydrofurfuryl acrylate).

Examples of the methacrylic esters include alkyl methacrylates (wherein alkyl groups each preferably has 1 to 10 carbon atoms) (such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, t-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl

methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, furfuryl methacrylate and tetrahydro-furfuryl methacrylate).

Examples of the acrylamide compounds include acrylamide, N-alkylacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, butyl, t-butyl, heptyl, octyl, cyclohexyl and hydroxyethyl), N,N-dialkylacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, butyl, isobutyl, ethylhexyl and cyclohexyl), N-hydroxyethyl-N-methylacrylamide and N-2-acetamidoethyl-N-acetylacrylamide.

Examples of the methacrylamide compounds include methacrylamide, N-alkylmethacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, t-butyl, ethylhexyl, hydroxyethyl and cyclohexyl), N,N-dialkylmethacrylamides (wherein alkyl groups are, for example, ethyl, propyl and butyl) and N-hydroxyethyl-N-methylmethacrylamide.

Examples of the allyl compounds include allyl esters (such as allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl

acetoacetate and allyl lactate) and allyloxyethanol.

Examples of the vinyl ethers include alkyl vinyl ethers (such as hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, butylaminoethyl vinyl ether, benzyl vinyl ether and tetrahydrofurfuryl vinyl ether).

Examples of the vinyl esters include vinyl butyrate, vinyl isobutyrate, vinyl trimethylacetate, vinyl diethylacetate, vinyl valerate, vinyl caproate, vinyl chloroacetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl acetoacetate, vinyl lactate, vinyl  $\beta$ -phenylbutyrate and vinyl cyclohexylcarboxylate.

The monomers also include dialkyl itaconates (such as dimethyl itaconate, diethyl itaconate and dibutyl itaconate), dialkyl esters of maleic acid or fumaric acid (such as dimethyl maleate and dibutyl fumarate) and monoalkylesters thereof, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic anhydride, maleimide, acrylonitrile, methacrylonitrile and maleylonitrile.

In addition, any monomers may be used, as long as they are addition-polymerizable unsaturated compounds copolymerizable

with the repeating structural units represented by general formula [I].

The content of the repeating structural units corresponding to the additional monomers as described above is preferably 99 mol% or less, more preferably 90 mol% or less, and most preferably 80 mol% or less, based on the total molar number of the repeating structural units represented by general formula [I] and the repeating structural units having alicyclic hydrocarbon moieties. Exceeding 99 mol% is unfavorable because the effect of the present invention is not sufficiently manifested.

The weight-average molecular weight of the above-mentioned resins used in the present invention is preferably 2,000 to 200,000. If the weight-average molecular weight is less than 2,000, deterioration in heat resistance and resistance to dry etching is unfavorably observed. Exceeding 200,000 brings about unfavorable results such as deterioration in developing properties and deterioration in film forming properties caused by an extreme increase in viscosity.

As described above, the resins used in the present invention have no groups strong in photoabsorption in the far ultraviolet region on either their main chains or their side chains, so that irradiated light sufficiently arrives at around the substrate sides of coated films, which causes high sensitivity and excellent pattern profiles. It goes without saying that being low in transmission density is a necessary condition and



does not necessarily results in excellent resist characteristics, and that other factors also have influence thereon. However, the resins used in the present invention fulfill this necessary condition.

The resins used in the present invention can be synthesized by usual methods including radical polymerization using azo compounds as initiators.

The positive type photoresist compositions of the present invention mainly contain the above-mentioned resins and photo acid generators. The amount of the resin added to the whole composition is 40% to 99% by weight, and preferably 50% to 97% by weight, based on the total solid content of the resist.

Then, the photo acid generators contained in the positive type photoresist compositions of the present invention are described below.

The photo acid generators are required to satisfy two properties, namely (1) transparency to exposure light (in the case that the agents have no photobleaching property) and (2) sufficient photodecomposability for ensuring resist sensitivity.

Although guidelines for molecular design for fulfilling such conflicting requirements are not clear in the present circumstances, examples of the photo acid generators include aliphatic alkylsulfonium salts having 2-oxocyclohexyl groups described in JP-A-7-25846, JP-A-7-28237, JP-A-7-92675 and JP-A-8-27102, and N-hydroxysuccinimide sulfonates. Further, examples thereof

include sulfonium salts represented by the following general formula (VI), disulfones represented by the following general formula (VII) and compounds represented by the following general formula (VIII), which are described in J. Photopolym. Sci. Technol., 7 (3), 423 (1994).



wherein  $R_{12}$  to  $R_{15}$ , which may be the same or different, each represents an alkyl group or a cyclic alkyl group.

Further, N-hydroxymaleiminide sulfonates represented by the following general formula (IX) are also preferred.



wherein  $R_{16}$  and  $R_{17}$ , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, or a cycloalkyl group having 6 or less carbon atoms, and  $R_{16}$  and  $R_{17}$  may combine together by an alkylene group to form a ring; and  $R_{18}$  represents an alkyl group, a perfluoroalkyl group,

a cycloalkyl group or a camphor substituent. Such N-hydroxymaleiminide sulfonates are particularly preferred in photosensitivity.

In the above-mentioned general formula (IX), the alkyl groups each having 1 to 6 carbon atoms represented by  $R_{16}$  and  $R_{17}$  include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl and n-hexyl. Particularly, methyl, ethyl and propyl are preferred, and methyl and ethyl are more preferred.

The cycloalkyl groups each having 6 or less carbon atoms include cyclopropyl, cyclopentyl and cyclohexyl. Cyclopentyl and cyclohexyl are preferred. Examples of the formation of rings with  $R_{16}$  and  $R_{17}$  by alkylene chains include the formation of cyclohexyl, norbornyl and tricyclodecanyl groups.

The alkyl groups represented by  $R_{18}$  include straight-chain alkyl groups each having 1 to 20 carbon atoms, including methyl, ethyl and propyl, and branched alkyl groups each having 1 to 20 carbon atoms, including isopropyl, isobutyl, tert-butyl and neopentyl. Straight-chain or branched alkyl groups each having 1 to 16 carbon atoms are preferred, and straight-chain or branched alkyl groups each having 4 to 15 carbon atoms are more preferred.

The perfluoroalkyl groups include straight-chain perfluoroalkyl groups each having 1 to 20, including trifluoromethyl and pentafluoroethyl, and branched perfluoroalkyl groups each having 1 to 20, including heptafluoroisopropyl and nonafluoro-tert-butyl. Straight-chain or branched perfluoroalkyl groups each having

1 to 16 carbon atoms are preferred. The cyclic alkyl groups include monocyclic alkyl groups such as cyclopentyl and cyclohexyl, and polycyclic alkyl groups such as decalyl, norbornyl and tricyclodecanyl.

The amount of such a photo acid generators added to the composition is preferably 0.1% to 20% by weight, more preferably 0.3% to 15% by weight, and most preferably 1% to 10% by weight, based on the total solid content of the positive type photoresist composition.

In the positive type photoresist compositions of the present invention, photo acid generators as described below may be used in combination, in addition to the above-mentioned photo acid generators.

The following photo acid generators which can be used in combination are added to the compositions preferably in an amount of not more than 2% by weight, and more preferably in an amount of not more than 1% by weight, per the solid content of the whole positive type photoresist composition.

Examples of such photo acid generators include diazonium salts described in S. I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974) and T. S. Bal et al., Polymer, 21, 423 (1980), ammonium salts described in U.S. Patents 4,069,055, 4,069,056 and Re 27,992, and JP-A-3-140140, phosphonium salts described in D. C. Necker et al., Macromolecules, 17, 2468 (1984), C. S. Wen et al., Tec. Ptoc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), U.S.

Patents 4,069,055 and 4,069,056, iodonium salts described in J. V. Crivello et al., Macromolecules, 10 (6), 1307 (1977), Chem. & Eng. News, Nov. 28, 31 (1988), European Patents 104,143, 339,049 and 410,201, JP-A-2-150848 and JP-A-2-296514, sulfonium salts described in J. V. Crivello et al., Polymer, J. 17, 73 (1985), J. V. Crivello et al., J. Org. Chem., 43, 3055 (1978), W. R. Watt et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J. V. Crivello et al., Polymer Bull., 14, 279 (1985), J. V. Crivello et al., Macromolecules, 14 (5), 1141 (1981), J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), European Patents 370,693, 161,881, 410,201, 339,049, 233,567, 297,443 and 297,442, U.S. Patents 3,902,114, 4,933,377, 4,760,013, 4,734,444 and 2,833,827, and German Patents 2,904,626, 3,604,580 and 3,604,581, selenonium salts described in J. V. Crivello et al., Macromolecules, 10 (6), 1307 (1977) and J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), onium salts such as arsonium salts described in C. S. Wen et al., Tec. Ptoc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), organic halogen compounds described in U.S. Patent 3,905,815, JP-B-46-4605 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-48-36281, JP-A-55-32070, JP-A-60-239736, JP-A-61-169835, JP-A-61-169837, JP-A-62-58241, JP-A-62-212401, JP-A-63-70243 and JP-A-63-298339, organic metal/organic halides described in K. Meier et al., J. Rad. Curing, 13 (4), 26 (1986), T. P. Gill et al., Inorg. Chem., 19, 3007 (1980), D. Astruc,

Acc. Chem. Res., 19 (12), 377 (1996) and JP-A-2-161445, photo acid generators having o-nitrobenzyl type protective groups described in S. Hayase et al., J. Polymer Sci., 25, 753 (1987), E. Reichmanis et al., J. Polymer Sci., Polymer Chem. Ed., 23, 1 (1985), Q. Q. Zhu et al., J. Photochem., 36, 85, 39, 317 (1987), B. Amit et al., Tetrahedron Lett., (24), 2205 (1973), D. H. R. Barton et al., J. Chem. Soc., 35, 71 (1965), P. M. Collins et al., J. Chem. Soc., Perkin I, 1695 (1975), M. Rudinstein et al., Tetrahedron Lett., (17), 1445 (1975), J. W. Walker et al., J. Am. Chem. Soc., 110, 7170 (1988), S. C. Busman et al., J. Imaging Technol., 11 (4), 191 (1985), H. M. Houlihan et al., Macromolecules, 21, 2001 (1988), P. M. Collins et al., J. Chem. Soc., Chem. Commun., 532 (1972), S. Hayase et al., Macromolecules, 18, 1799 (1985), E. Reichmanis et al., J. Electrochem. Soc., Solid State Sci. Technol., 130 (6), F. M. Houlihan et al., Macromolecules, 21, 2001 (1988), European Patents 290,750, 046,083, 156,535, 271,851 and 388,343, U.S. Patents 3,901,710 and 4,181,531, JP-A-60-198538 and JP-A-53-133022, compounds producing sulfonic acids by photolysis which are represented by iminosulfonates described in M. Tunooka et al., Polymer Preprints Japan, 35 (8), G. Berner et al., J. Rad. Curing, 13 (4), W. J. Mijs et al., Coating Technol., 55 (697), 45 (1983), Akzo, H. Adachi et al., Polymer Preprints Japan, 37 (3), European Patents 199,672, 84,515, 44,115, 618,564, and 101,122, U.S. Patents 618,564, 4,371,605 and 4,431,774, JP-A-64-18143, JP-A-2-245756 and JP-A-3-140109, and disulfone

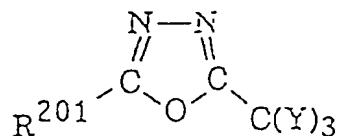
compounds described in JP-A-61-166544.

Further, compounds in which these groups or compounds generating acids with light are introduced into their main chains or side chains can be used. Examples of such compounds are described in M. E. Woodhouse et al., J. Am. Chem. Soc., **104**, 5586 (1982), S. P. Pappas et al., J. Imaging Sci., **30** (5), 218 (1986), S. Kondo et al., Makromol. Chem., Rapid Commun., **9**, 625 (1988), Y. Yamada et al., Makromol. Chem., 152, 153, 163 (1972), J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., **17**, 3845 (1979), U.S. Patent 3,849,137, German Patent 3,914,407, JP-A-63-26653, JP-A-55-164824, JP-A-62-69263, JP-A-63-146038, JP-A-63-163452, JP-A-62-153853 and JP-A-63-146029.

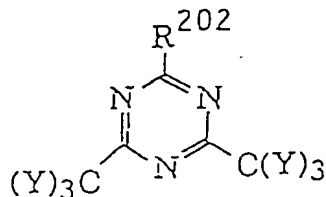
Further, compounds generating acids with light can also be used which are described in V. N. R. Pillai Synthesis, (1) 1 (1980), A. Abad et al., Tetrahedron Lett., (47), 4555 (1971), D. H. R. Barton et al., J. Chem. Soc., (C), 329 (1970), U.S. Patent 3,779,778 and European Patent 126,712.

Of the above-mentioned compounds which can be used in combination and are decomposed by irradiation of active light rays or radiation to generate acids, compounds particularly effectively used are described below.

(1) Oxazole derivatives substituted by trihalomethyl groups, which are represented by the following general formula (PAG1), or S-triazine derivatives represented by the following general formula (PGA2)



(PAG1)

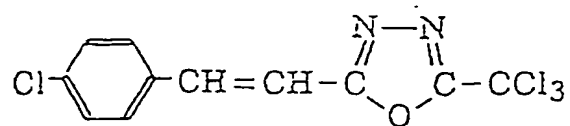


(PGA2)

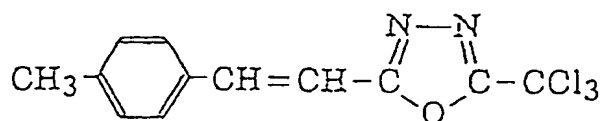
wherein  $R^{201}$  represents a substituted or unsubstituted aryl or alkenyl group;  $R^{202}$  represents a substituted or unsubstituted aryl, alkenyl or alkyl group, or  $-C(Y)_3$ ; and Y represents a chlorine atom or a bromine atom.

Specific examples thereof include but are not limited to the following compounds:

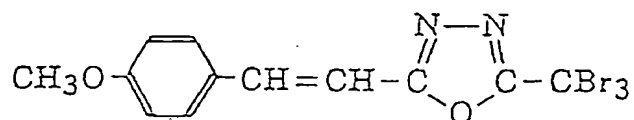




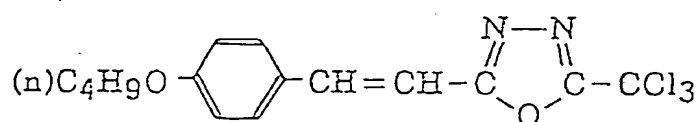
(PAG1-1)



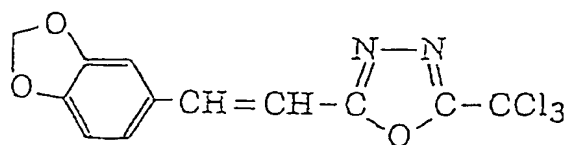
(PAG1-2)



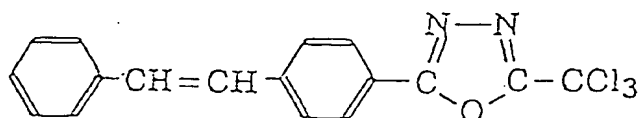
(PAG1-3)



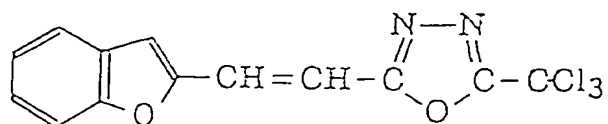
(PAG1-4)



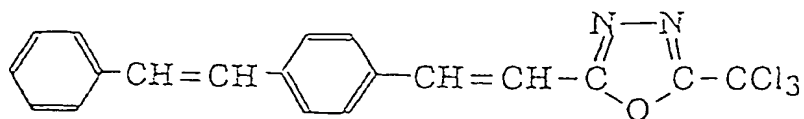
(PAG1-5)



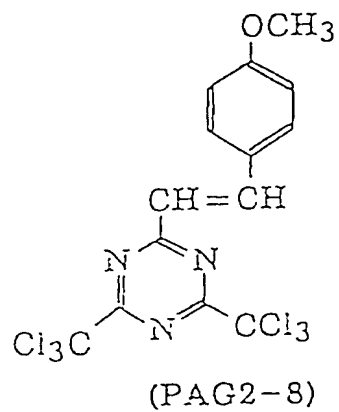
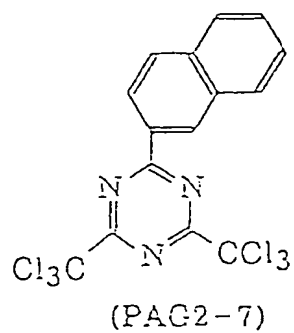
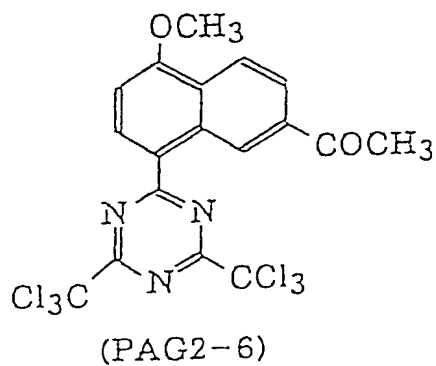
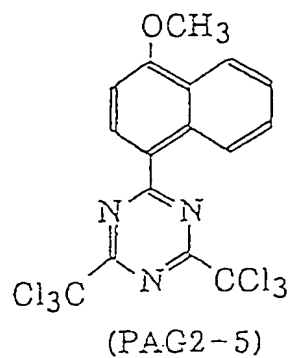
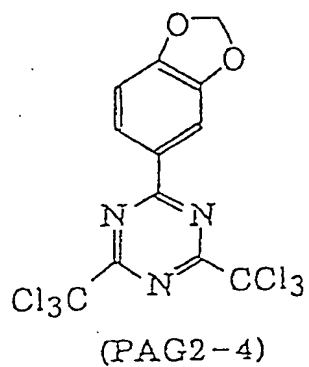
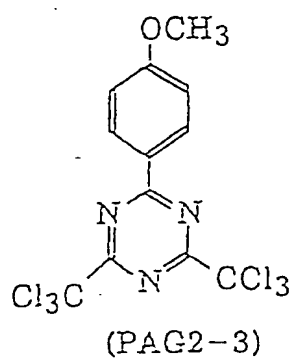
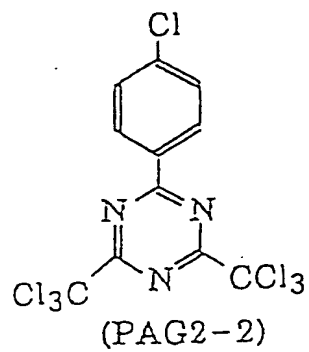
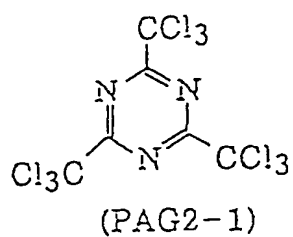
(PAG1-6)

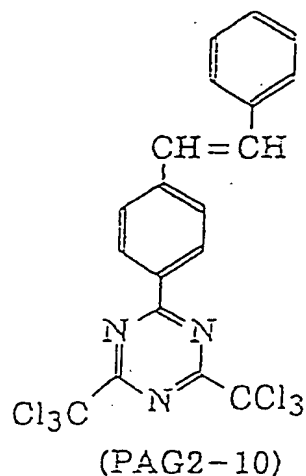
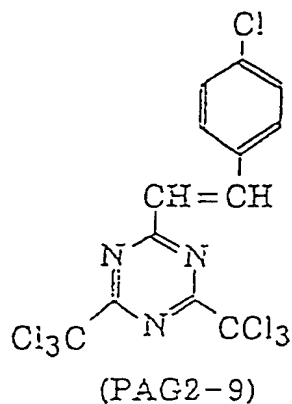


(PAG1-7)

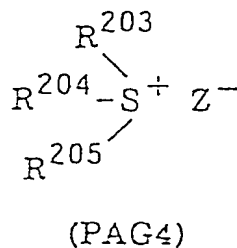
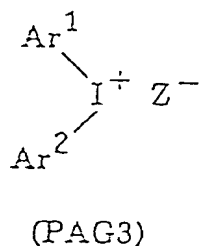


(PAG1-8)





(2) Iodonium salts represented by the following general formula (PAG3) or sulfonium salts represented by the following general formula (PAG4)



wherein  $Ar^1$  and  $Ar^2$  each independently represents a substituted or unsubstituted aryl group. Preferred examples of the substituent groups include alkyl, haloalkyl, cycloalkyl, aryl, alkoxy, nitro, carboxyl, alkoxy carbonyl, hydroxyl, mercapto and halogen atoms.

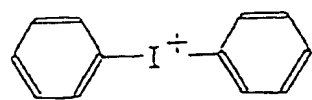
$R^{203}$ ,  $R^{204}$  and  $R^{205}$  each independently represents a substituted or unsubstituted alkyl or aryl group, and preferably

an aryl group having 6 to 14 carbon atoms, an alkyl group having 1 to 8 carbon atoms or a substituted derivative thereof. Preferred examples of the substituent groups for aryl include alkoxyl of 1 to 8 carbon atoms, alkyl of 1 to 8 carbon atoms, nitro, carboxyl, hydroxyl and halogen atoms, and preferred examples thereof for alkyl include alkoxyl of 1 to 8 carbon atoms, carboxyl and alkoxycarbonyl.

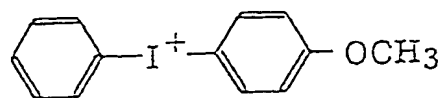
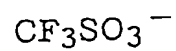
$Z^-$  represents a counter ion such as a perfluoroalkane-sulfonic acid anion, for example,  $CF_3SO_3^-$ , or a pentafluoro-benzenesulfonic acid anion.

Two of  $R^{203}$ ,  $R^{204}$  and  $R^{205}$ , and  $Ar^1$  and  $Ar^2$  may combine together by each single bond or substituent group.

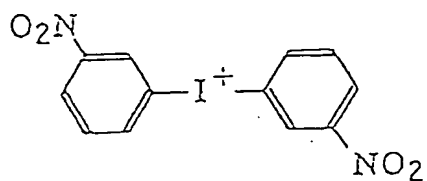
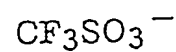
Specific examples thereof include but are not limited to the following compounds:



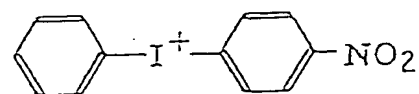
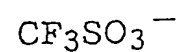
(PAG3-1)



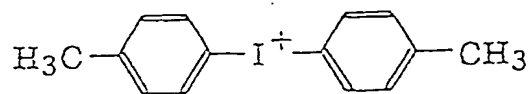
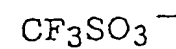
(PAG3-2)



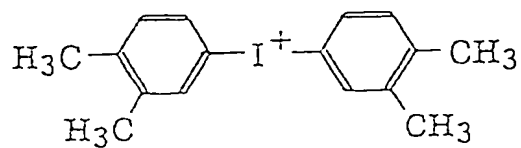
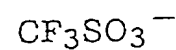
(PAG3-3)



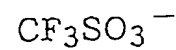
(PAG3-4)

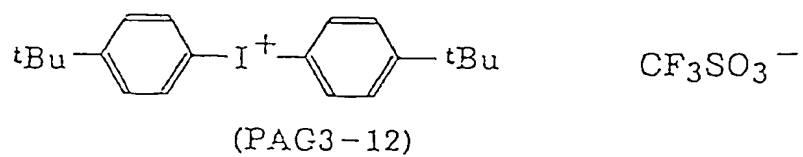
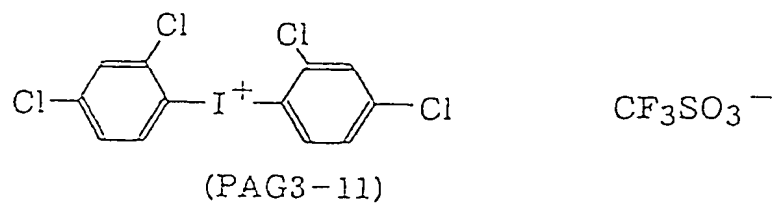
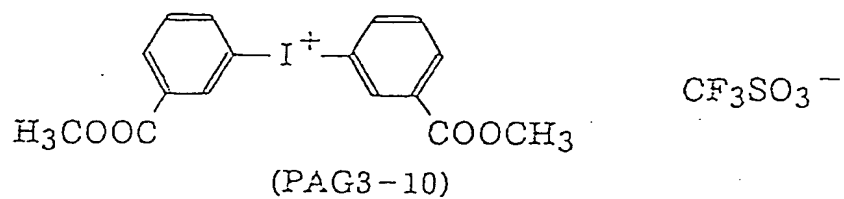
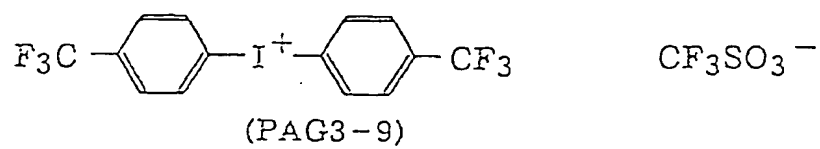
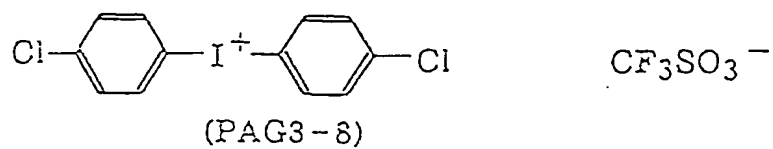
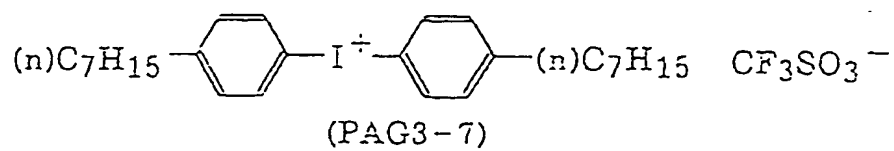


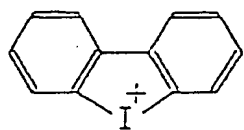
(PAG3-5)



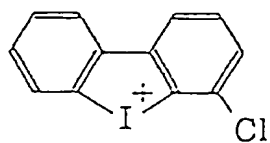
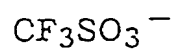
(PAG3-6)



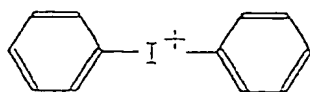
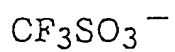




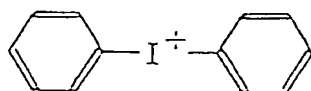
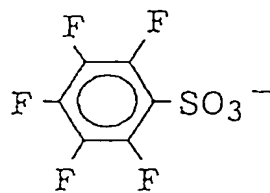
(PAG3-13)



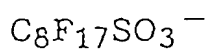
(PAG3-14)

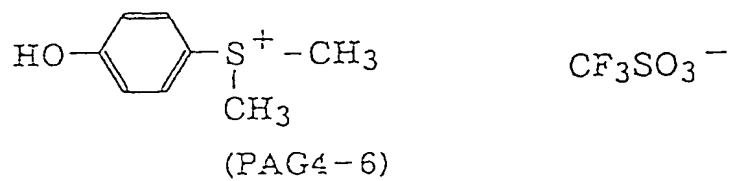
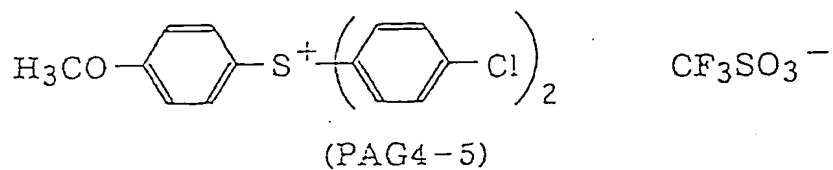
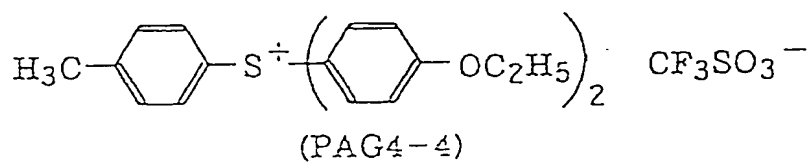
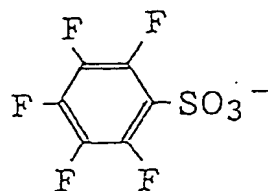
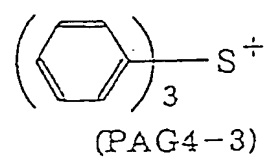
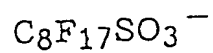
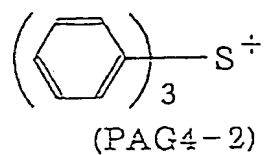
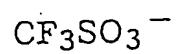
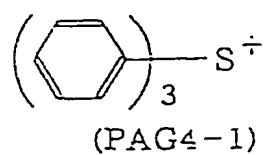


(PAG3-15)

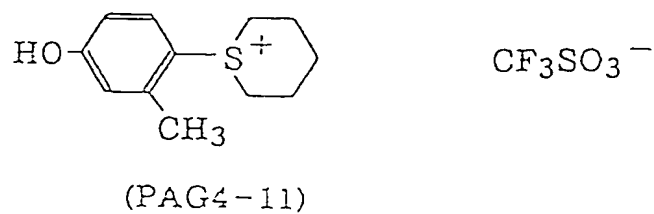
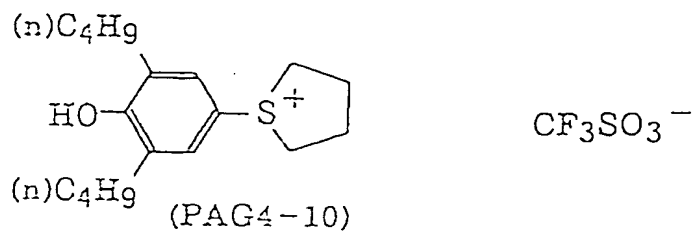
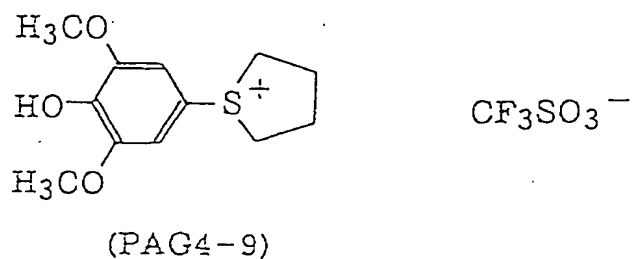
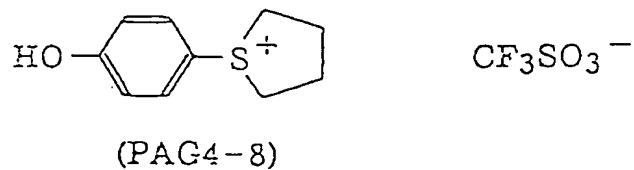
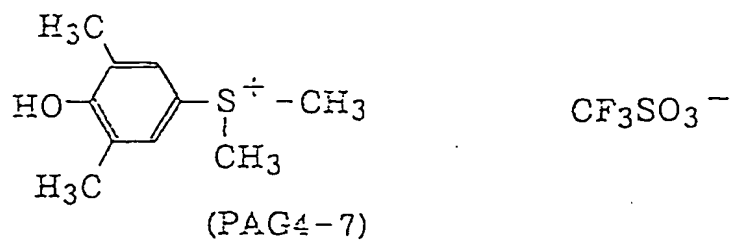


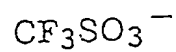
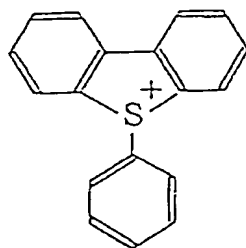
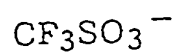
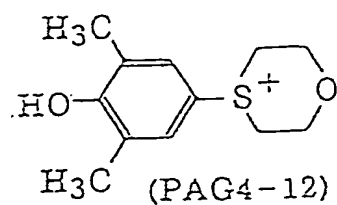
(PAG3-16)



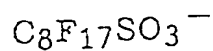
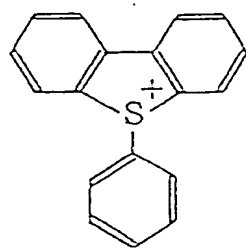




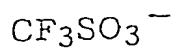
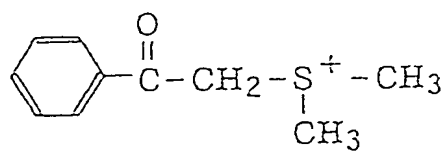




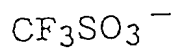
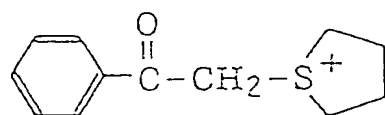
(PAG4-13)



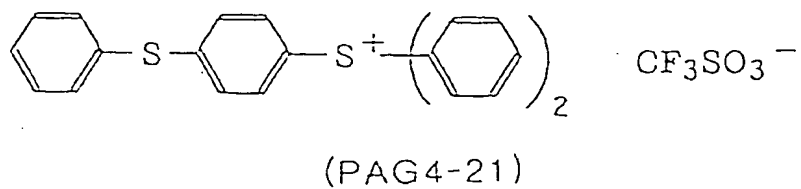
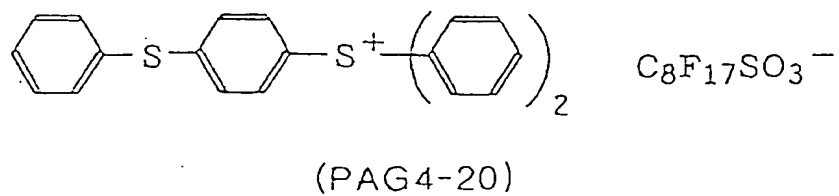
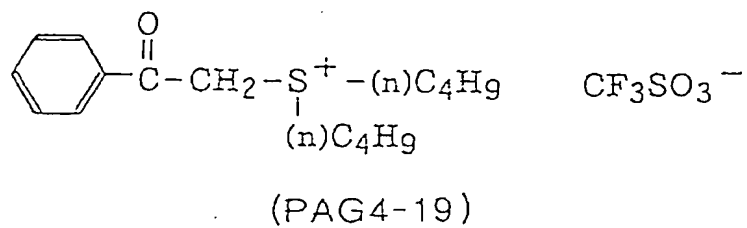
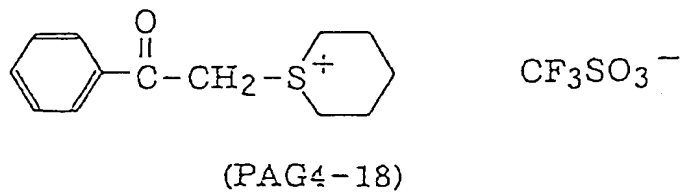
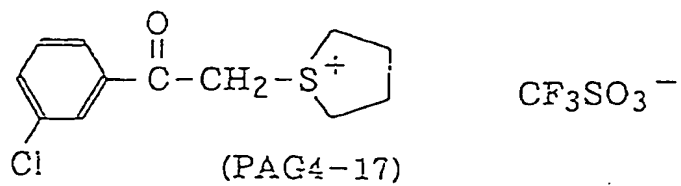
(PAG4-14)

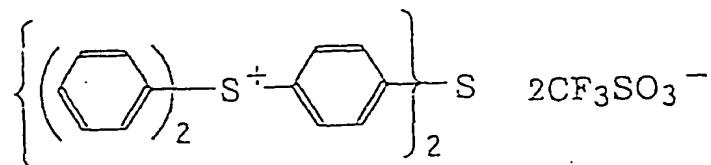


(PAG4-15)

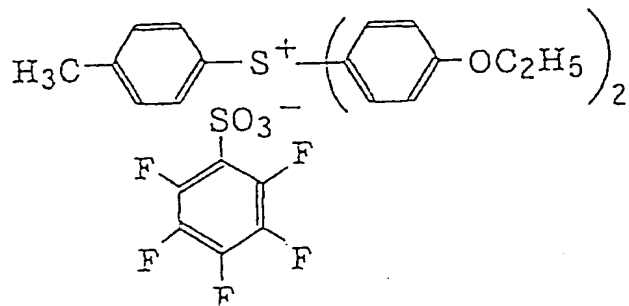


(PAG4-16)

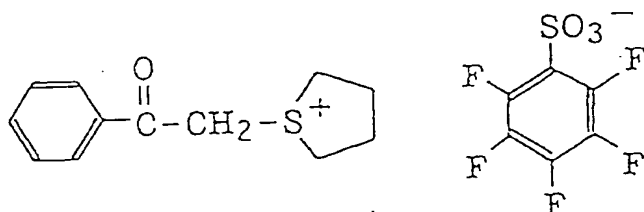




(PAG4-22)



(PAG4-23)

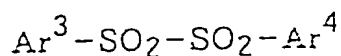


(PAG4-24)

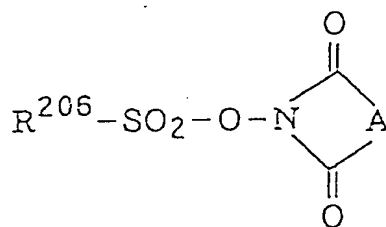
The above-mentioned onium salts represented by general formulas (PAG3) and (PAG4) are known, and can be synthesized, for example, by methods described in J. W. Knapczyk et al., J. Am. Chem. Soc., **91**, 145 (1969), A. L. Maycok et al., J. Org. Chem., **35**, 2532 (1970), E. Goethas et al., Bull. Soc. Chem. Belg., **73**, 546 (1964), H. M. Leicester, J. Am. Chem. Soc., **51**, 3587 (1929), J. V. Crivello et al., J. Polymer Chem. Ed., **18**, 2677

(1980), U.S. Patents 2,807,648 and 4,247,473, and JP-A-53-101331.

(3) Disulfone derivatives represented by the following general formula (PAG5) or iminosulfonate derivatives represented by the following general formula (PAG6)



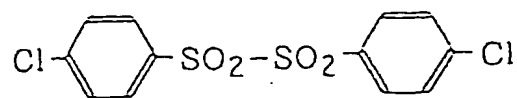
(PAG5)



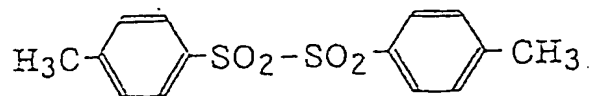
(PAG6)

wherein  $\text{Ar}^3$  and  $\text{Ar}^4$  each independently represents a substituted or unsubstituted aryl group;  $\text{R}^{206}$  represents a substituted or unsubstituted alkyl or aryl group; and A represents a substituted or unsubstituted alkylene, alkenylene or arylene group.

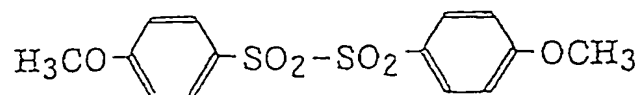
Specific examples thereof include but are not limited to the following compounds:



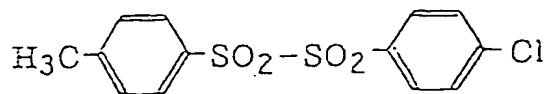
(PAG5-1)



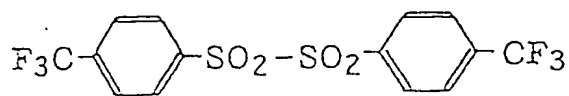
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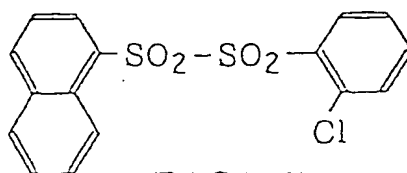
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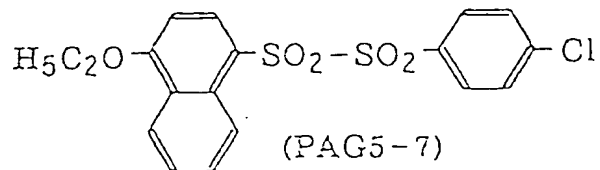
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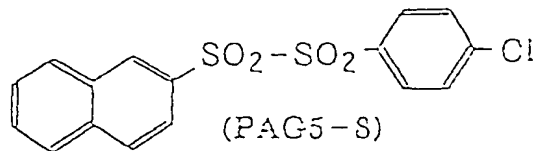
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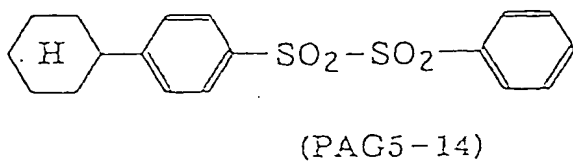
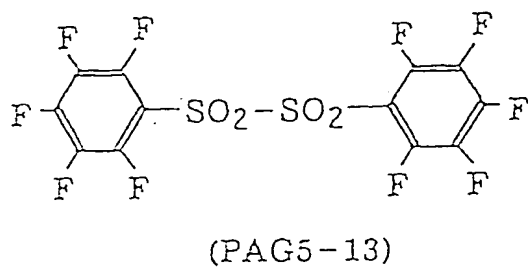
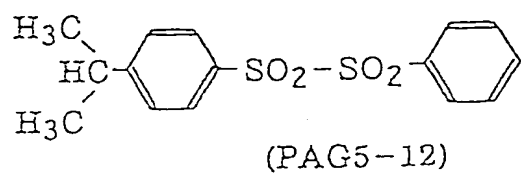
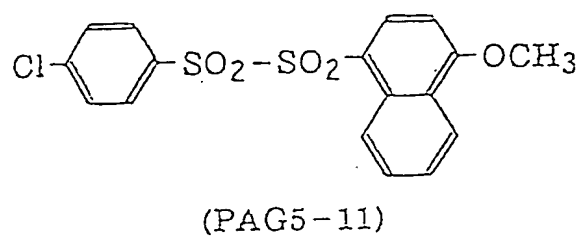
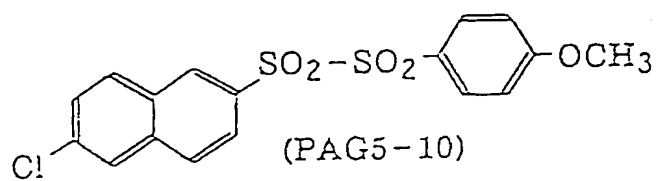
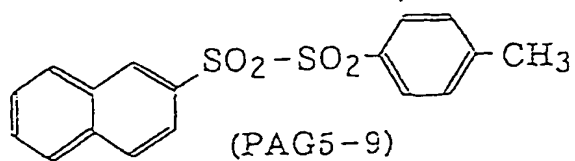
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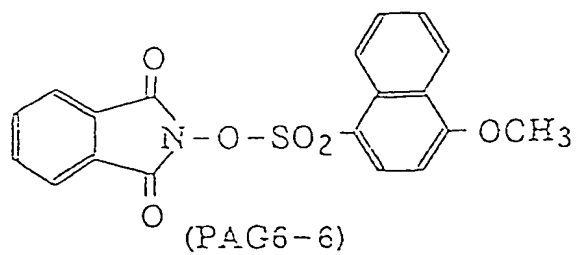
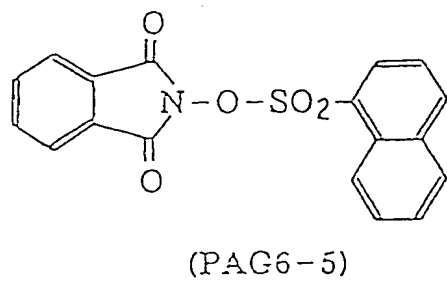
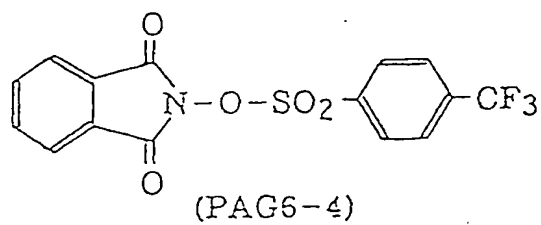
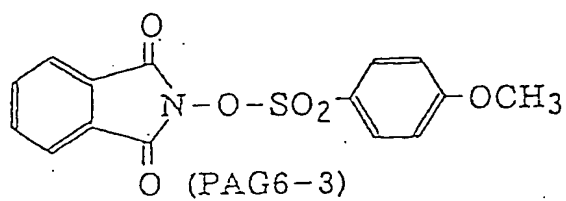
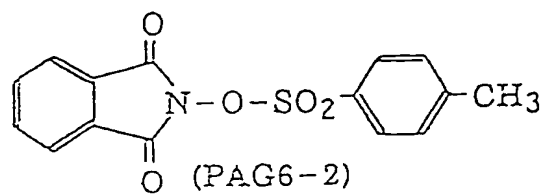
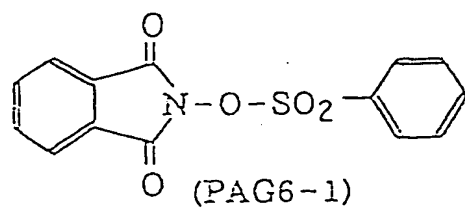


(PAG5-7)

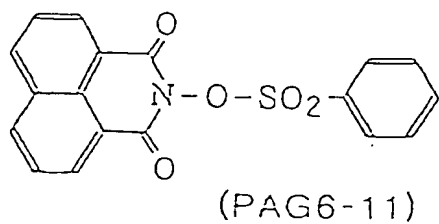
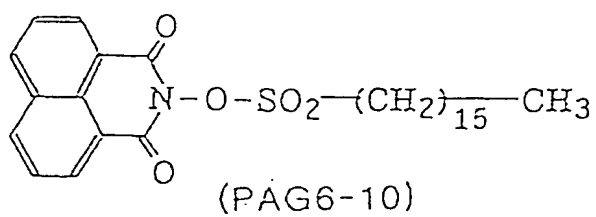
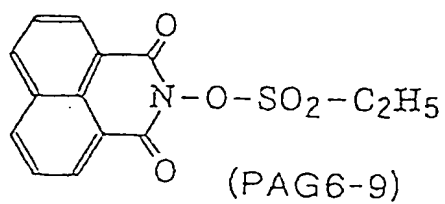
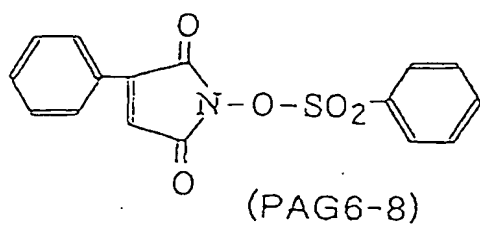
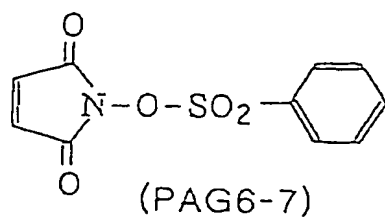


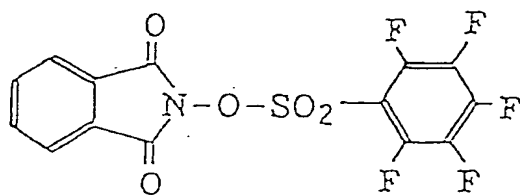
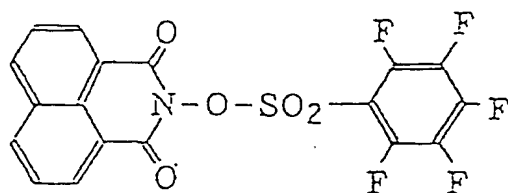
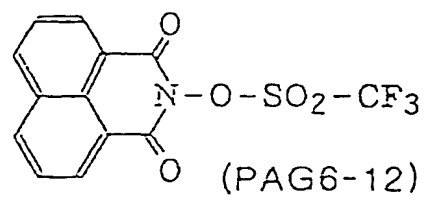
(PAG5-8)











Appropriate alkali-soluble low molecular weight compounds may be added to the positive type photoresist compositions for improving alkali solubility in the systems or controlling the glass transition temperature of the systems to prevent the films from becoming brittle and the heat resistance from being deteriorated. The alkali-soluble low molecular weight compounds include compounds having acidic groups in their molecules such as dialkylsulfonamide compounds, dialkylsulfonylimide ( $-\text{SO}_2-\text{NH}-\text{CO}-$ ) compounds and dialkyldisulfonylimide ( $-\text{SO}_2-\text{NH}-\text{SO}_2-$ ) compounds. The content of the alkali-soluble low molecular weight compound is preferably 40% by weight or less, more preferably 30% by weight or less, and most preferably 25% by weight or less, based on the binder resin.

The compositions of the present invention are preferably used as solutions thereof in specific solvents. Such solvents may be any, as long as they are organic solvents which sufficiently dissolve the respective solid components and can provide the solutions forming uniform coated films by methods such as spin coating. Further, they may be used alone or as a mixture of two or more of them. Specific examples thereof include but are not limited to n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, t-butyl alcohol, methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monoethyl ether acetate, methyl lactate, ethyl lactate, 2-methoxybutyl acetate, 2-ethoxyethyl acetate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate,

ethyl 3-methoxypropionate, N-methyl-2-pyrrolidinone, cyclohexanone, cyclopentanone, cyclohexanol, methyl ethyl ketone, 1,4-dioxane, ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, ethyleneglycol monoisopropyl ether, diethyleneglycol monomethyl ether, diethylene glycol dimethyl ether and 2-heptanone.

The positive type photoresist compositions of the present invention may further contain other components such as surfactants, pigments, stabilizers, coating improvers and dyes, if necessary.

Such positive type photoresist compositions of the present invention are applied onto substrates to form thin films. The thickness of the coated films is preferably 0.4  $\mu\text{m}$  to 1.5  $\mu\text{m}$ .

As exposure means, ones in which the exposure wavelength is included within the range of 170 nm to 220 nm, such as ArF excimer laser stepper exposure, are preferred, and ArF excimer laser stepper exposure is particularly preferred.

#### [Examples]

The present invention will hereinafter be described in more detail by reference to examples. However, the present invention is not limited thereto.

### SYNTHESIS EXAMPLE 1

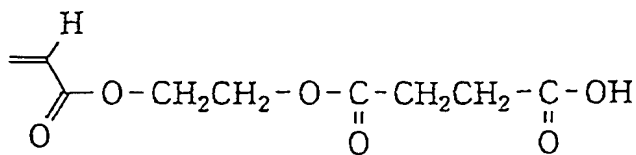
#### Synthesis of Monomer [I-A-1]

Acrylic acid (72 g) was dissolved in 500 ml of dichloromethane, and 10 g of 4-dimethylaminopyridine was added thereto. Further, 1-chloro-2-methyl-2-propanol was gently added. The resulting solution was cooled on an ice bath, and 25 g of dicyclohexylcarbodiimide was further slowly added thereto. After stirring as such for 30 minutes, the ice bath was removed, and the temperature was spontaneously elevated to room temperature, followed by stirring at room temperature for 3 hours. After the reaction was completed, the precipitated powder was filtered, and the resulting filtrate was extracted with 10% aqueous hydrochloric acid. The extract was washed with an aqueous solution of sodium bicarbonate, and further with saturated saline. The resulting oil layer was concentrated, and purified by silica gel column chromatography to obtain 145 g of the desired monomer [I-A-1].

### SYNTHESIS EXAMPLE 2

#### Synthesis of Monomer [I-C-1]

Monomer [I-C-1] was synthesized in the same manner as with Synthesis Example 40 with the exception that the following carboxylic acid monomer was used in place of acrylic acid:



### SYNTHESIS EXAMPLE 3

#### Synthesis of Monomer [I-D-1]

Monomer [I-D-1] was synthesized in the same manner as with Synthesis Example 40 with the exception that Aronix M-5600 manufactured by Toagosei Co., Ltd. was used in place of acrylic acid.

### SYNTHESIS EXAMPLE 4

#### Synthesis of Resin A

Tricyclodecanyl methacrylate (22.0 g), monomer [I-A'-1] (13.0 g) and acrylic acid (1.4 g) were dissolved in THF (85 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 100 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 100 g of THF was reprecipitated with a mixed solvent of 2 liters of distilled water/2 liters of methanol, thus recovering the desired resin A as a white powder.

The GPC analysis of the resulting copolymer showed that

it had a weight-average molecular weight of 18,000 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 5

##### Synthesis of Resin B

Tricyclodecanyl methacrylate (22.0 g), monomer [I-C-1] (24.5 g) and acrylic acid (1.4 g) were dissolved in THF (112 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 150 g of THF was reprecipitated with a mixed solvent of 3 liters of distilled water/3 liters of methanol, thus recovering the desired resin B as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 19,200 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 6

##### Synthesis of Resin C

Tricyclodecanyl methacrylate (22.0 g), monomer [I-D-1] (21.1 g) and acrylic acid (1.4 g) were dissolved in THF (104 g), and then, the reaction solution was heated to 65°C while

passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 150 g of THF was reprecipitated with a mixed solvent of 3 liters of distilled water/2 liters of methanol, thus recovering the desired resin C as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 18,800 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 7

##### Synthesis of Resin D

Tricyclodecanyl methacrylate (22.0 g), t-butyl acrylate (10.3 g) and acrylic acid (1.4 g) were dissolved in THF (80 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 100



g of THF was reprecipitated with a mixed solvent of 2 liters of distilled water/2 liters of methanol, thus recovering the desired resin D as a white powder.

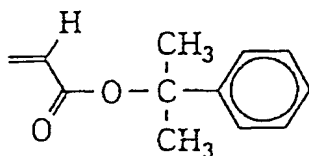
The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 17,800 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 8

##### Synthesis of Resin E for Comparison

Tricyclodecanyl methacrylate (22.0 g), the following monomer a (11.2 g) and acrylic acid (1.4 g) were dissolved in THF (90 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 100 g of THF was reprecipitated with a mixed solvent of 3 liters of distilled water/3 liters of methanol, thus recovering the desired resin E as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 18,600 in terms of standard polystyrene.



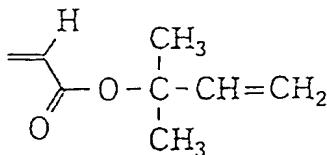
(a)

### SYNTHESIS EXAMPLE 9

#### Synthesis of Resin F for Comparison

Tricyclodecanyl methacrylate (22.0 g), the following monomer b (11.2 g) and acrylic acid (1.4 g) were dissolved in THF (90 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 100 g of THF was reprecipitated with a mixed solvent of 3 liters of distilled water/3 liters of methanol, thus recovering the desired resin F as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 18,300 in terms of standard polystyrene.



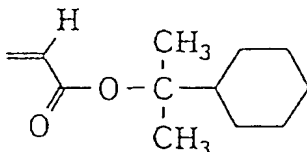
(b)

### SYNTHESIS EXAMPLE 10

#### Synthesis of Resin G for Comparison

Tricyclodecanyl methacrylate (22.0 g), the following monomer c (15.9 g) and acrylic acid (1.4 g) were dissolved in THF (95 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 120 g of THF was reprecipitated with a mixed solvent of 3 liters of distilled water/3 liters of methanol, thus recovering the desired resin G as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 18,400 in terms of standard polystyrene.



(c)

### SYNTHESIS EXAMPLE 11

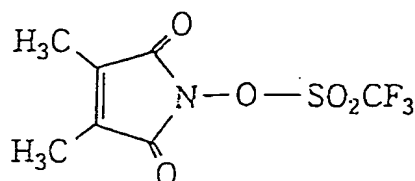
#### Synthesis of Photo Acid Generator (1)

Sodium hydroxide (8 g) and hydroxylamine hydrochloride (14 g) were dissolved in 200 ml of distilled water, and 25 g of dimethylmaleic anhydride added thereto. Then, the resulting solution was stirred at room temperature for 5 hours, followed by heat stirring at 100°C for 3 hours. After the reaction was completed, aqueous hydrochloric acid was added to the reaction solution. Then, the resulting solution was further saturated with sodium chloride, and thereafter extracted with ethyl acetate.

The procedure of concentrating the extracted ethyl acetate solution to one third, adding toluene to the concentrated solution and reconcentrating the solution to which toluene was added was repeated to isolate 15 g of N-hydroxymaleiminide.

In dichloromethane, 4.2 g of N-hydroxymaleiminide thus synthesized was dissolved, and 8.5 g of trifluoromethane-sulfonic acid anhydride was added dropwise on an ice bath for 1 hour. After 2.8 g of pyridine was further added dropwise for 2 hours, the ice bath was removed, and the temperature was elevated to room temperature, followed by stirring as such for 10 hours. After the reaction was completed, the reaction solution was washed with distilled water, and concentrated to conduct crystallization in hexane. The hexane layer was concentrated to obtain 10 g of the desired compound.

The following structure was confirmed by <sup>13</sup>CNMR:



### EXAMPLES AND COMPARATIVE EXAMPLES

In 2-heptanone, 1.2 g of each of resins A to G synthesized in Synthesis Examples described above and 0.25 g of photo acid generator (1) were dissolved so as to give a solid content of 14% by weight, and then, the resulting solution was filtered through a 0.1- $\mu$ m microfilter to prepare a positive type photoresist composition solution.

#### (Evaluation Tests)

The resulting positive type photoresist composition solution was applied onto a silicon wafer with a spin coater, and dried at 120°C for 90 seconds to prepare a positive type photoresist film having a thickness of about 0.5  $\mu$ m, which was exposed to an ArF excimer laser beam (193 nm). After exposure, heat treatment was carried out at 110°C for 90 seconds. Then, the photoresist film was developed with a 2.38% aqueous solution of tetramethylammonium hydroxide, and rinsed with distilled water to obtain a resist pattern profile.

#### [Relative Sensitivity]

Taking as a sensitivity an exposure which could reproduce a pattern having a width of 0.5  $\mu$ m, and taking the resist sensitivity

of Example 1 as 1, the relative sensitivity of a resist other than that of Example 1 was determined by the following equation:

$$\frac{\text{Sensitivity other than that of Example 1}}{\text{Sensitivity of Example 1}}$$

[Pattern Profile]

The resist pattern profile obtained above was observed under a scanning electron microscope, and one showing a rectangular form was rated as O and one showing a T-top form as x.

[Adhesion]

Minimum Width of Remaining Thin Line: The resist pattern profile obtained above was observed under a scanning electron microscope, and the adhesion was evaluated by the width of the thinnest remaining line.

Results thereof are shown in Table 1.

TABLE 1

	<u>Resin Used</u>	<u>Relative Sensiti- vity</u>	<u>Pattern Profile</u>	<u>Minimum Width of Remain- ing Thin Line</u>
Example 1	A4	1.0	O	0.30
Example 2	B4	1.0	O	0.29
Example 3	C4	1.1	O	0.31
Comparative Example 1	D4	1.7	x	0.50
Comparative Example 2	E4	2.1	x	0.45
Comparative Example 3	F4	1.6	x	0.48
Comparative Example 4	G4	1.5	x	0.48

[Transmission Density]

The same composition as that of the positive type photoresist composition solution applied onto the silicon wafer for the above-mentioned tests was applied onto a silica plate having no photoabsorption in the far ultraviolet region to prepare a sample for density measurement. The spectral adsorption in the far ultraviolet region was measured using a spectral densitometer to determine a transmission density at 193 nm, which was divided by a thickness of the coated layer of the sample to determine a transmission density per micron of coated layer

in thickness.

Results thereof are shown in Table 2.

TABLE 2

	<u>Resin Used</u>	<u>Transmission Density</u>
Example 1	A	0.16
Example 2	B	0.17
Example 3	C	0.20
Comparative Example 1	D	0.16
Comparative Example 2	E	1.10
Comparative Example 3	F	0.17
Comparative Example 4	G	0.68

Referring to Table 1, Comparative Examples 10 to 13 each has problems in the relative sensitivity, the pattern profile and the adhesion. On the other hand, Examples 1 to 3 relating to the positive type photoresist compositions of the present invention are at levels satisfying all of them. That is, of the resins in which the acid decomposable groups are attached by ester linkages to tertiary carbon, the resins of the present invention, namely resins each having the structure that tertiary carbon is substituted by a halomethylene group, are particularly



suitable for lithography using far ultraviolet rays including ArF excimer laser exposure.

On the other hand, Table 2 shows that all sample resins A4 to C4 of the present invention have a transmission density of 0.4 or less per micron of coated layer in thickness at 193 nm, and sufficiently low in photoabsorption to exposure for patterning compared with the samples for comparison. This means that light reaches the substrate side of a composition layer by irradiation without significant attenuation, and is reflected in the good pattern profile and the high relative sensitivity shown in Table 1. In Comparative Examples 1 and 4, the resins low in transmission density are used, but is nevertheless inferior to the samples of the present invention in the photoresist characteristics shown in Table 1. This means that being low in transmission density is a necessary condition which the characteristics of the photoresists for far ultraviolet rays should possess, but not a sufficient condition.

[Effect of the invention]

As described above, according to the present invention, there can be provided positive photoresist compositions which are sufficiently suitable, particularly, for light in the wavelength region of 170 nm to 220 nm, high in sensitivity, excellent in adhesion and can give good resist pattern profiles.

[Name of document] ABSTRACT

[Summary]

[Subject]

The absorbance be low, that is to say, high sensitivity to far ultraviolet ray, especially ArF excimer laser source of light and it along with the development of an excellent photoresist composition even focus permission degree, resolution, pattern profile make a purpose.

[Solution means]

It is the positive type photoresist composition for far ultraviolet ray exposure as the characteristic that contains a polymer having as one of repeating units a monomer containing a specific acid decomposable group having a halogen atom substituent and a tertiary carbon and a compound generating an acid by irradiation of an active light or radiation.

[Chosen drawing] None